

Additive Methods for Prediction of Thermochemical Properties. The Laidler Method Revisited. 1. Hydrocarbons

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(Received 26 October 2004; revised manuscript received 18 February 2005; accepted 1 May 2005; published online 30 December 2005)

A new parameterization of the Laidler method for estimation of atomization enthalpies and standard enthalpies of formation at 298.15 K for several families of hydrocarbons (alkanes, alkenes, alkynes, polyenes, poly-yenes, alkyl radicals, cycloalkanes, cycloalkenes, benzene derivatives, and polyaromatics) is presented. A total of 200 compounds (164 for liquid phase) are used for the calculation of the parameters. Comparison between the experimental values and those calculated using the group additive scheme led to an average difference of $1.28 \text{ kJ} \cdot \text{mol}^{-1}$ for the gas phase enthalpy of formation (excluding the polyaromatic compounds) and of $1.38 \text{ kJ} \cdot \text{mol}^{-1}$ for the liquid phase enthalpy of formation. The data base used appears to be essentially error free, but for some compounds (e.g., 2,2,4-trimethyl-pentane, with the highest deviation among all compounds except the polyaromatic ones) the experimental values might need a reevaluation. An Excel worksheet is provided to simplify the calculation of enthalpies of formation and atomization enthalpies based on the Laidler terms defined in this paper. © 2006 American Institute of Physics. [DOI: 10.1063/1.1996609]

Key words: additive methods; atomization enthalpy; bond dissociation enthalpy; bond strength; enthalpy of formation; hydrocarbons; Laidler method.

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1. Introduction

Additive methods for estimation of thermochemical properties have been widely used.^{1–8} They are simple to apply, do not require significant computing power, and usually provide very reliable data. However additivity rules are not strictly applied to any physical property. The prediction of very accurate data often demands a number of “corrections,” which in turn require a large amount of values of the property to parameterize the method. Incidentally, this is another drawback of additivity methods: their empirical nature requires a reliable (experimental and/or computational) data collection.

With regard to thermodynamic quantities, the standard enthalpy of formation ($\Delta_f H^\circ$) is a key property. Another useful

quantity is the atomization enthalpy ($\Delta_{\text{atom}} H^\circ$), i.e., the enthalpy required to break all the bonds in a given molecule [reaction (1)]. The atomization enthalpy can be estimated as a sum of the “bond enthalpies” in the molecule



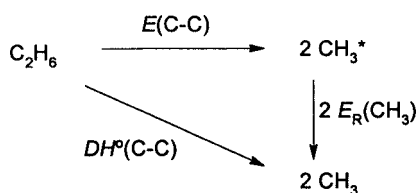
Several additivity methods have been developed to estimate enthalpies of formation and atomization enthalpies. The most frequently used is known as the Benson group method, which was proposed in 1958 by Benson and Buss.³ The parameters of Benson method have been refined and extended by many authors.⁶ Another method (or “scheme”) that is simple to use and very attractive to chemists, since it deals with bond enthalpies, is known as the Laidler method.² Here the parameters are assigned to the chemical bonds, and therefore should reflect the strengths of those bonds. In addition, the parameters can in principle be related to other properties, such as bond lengths. In the original formulation, for alkanes, Laidler defined one parameter for the C–C bond and three parameters for C–H bonds (depending if the carbon is a primary, secondary, or tertiary). When the Laidler method was proposed in 1956, it was important to keep the number of parameter as low as possible in order to minimize the calculation time. However, this is not a limitation today and some schemes use as many as 20 parameters for alkanes.⁷

The Laidler method has been refined by Tatevski⁹ but only for alkanes. In the present paper, a new parameterization of the Laidler method is proposed for the standard enthalpies of formation (gas and liquid phase) and atomization enthalpies of alkanes, alkenes, alkynes, polyenes, polyines, alkyl radicals, cycloalkanes, cycloalkenes, benzene derivatives, and polyaromatic hydrocarbons. This new parameterization improves the reliability of estimates (even for very large and bulky compounds) and allows, for the first time, the association of a physical meaning to the parameter values.

2. The Method Used

The main guidelines for the present parameterization were: (1) accuracy should not be sacrificed by imposing a limit to the number of parameters; and (2) the parameters meaning should be as clear as possible and easy to identify.

With regard to the method to evaluate the parameters, two approaches were considered: (1) to calculate all the parameters involved in a variety of families of compounds by a global regression analysis, or (2) to calculate the parameters for a basic set of compounds, e.g., alkanes, and then add sequentially new parameters for other families of compounds, keeping the ones already calculated as constants. Despite the fact that the later approach can simplify the introduction of new parameters, it could also lead to an inconsistent set of parameters if several families were sequentially added. The advantage of the first approach is to keep all the parameters consistent with each other, but requires that for every new family of compounds added all the parameters



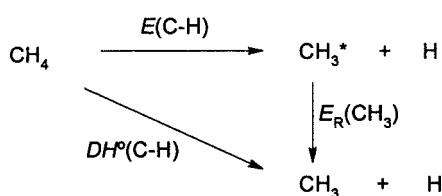
Scheme 1

must be optimized again. However, any desktop computer can optimize a large set of parameters in a few seconds. Therefore, approach (1) was our choice.

For the multiparameter regression analysis the MICROSOFT EXCEL 2000 Solver Tool was used. The estimates were made by the tangent method and forward derivatives with Newton search.

With a large set of parameters the regression can find several very close minima which, however, correspond to rather different values for the parameters. This is irrelevant for the enthalpies of formation since the parameters do not have a physical meaning. In the present paper, a starting value of zero was assigned to all the parameters concerning enthalpies of formation. By doing so, it was expected to arrive at a set of parameters whose values are as small as possible. The choice of parameters for the atomization should be more careful because, as stated above, $\Delta_{\text{atom}}H^\circ$ reflects the sum of all bond enthalpies in a molecule. Therefore, the parameters should have some physical meaning and be related to the bond strengths. To achieve this goal, an educated guess of the initial values must be made, or some initial restrictions have to be imposed in order to arrive at a sensible minimum. To keep the obtained results independent of the initial guess some restrictions were imposed in a first step, as explained in the next paragraphs.

Consider Schemes 1 and 2, where an asterisk means that the fragment retains the same geometrical arrangement it had in the parent molecule. The experimental bond dissociation enthalpies, $DH^\circ(\text{C-C})$ and $DH^\circ(\text{C-H})$, which can be calculated from the experimental enthalpies of formation of the involved species, are related to the bond enthalpy terms $E(\text{C-C})$ and $E(\text{C-H})$ through the reorganization enthalpies (E_R), due to the relaxation of the fragment after the bond cleavage.¹⁰ We assume that the values of $E(\text{C-C})$ and $E(\text{C-H})$ can be identified with the respective Laidler terms (E_L) defined for the fitting. Although this assumption is not true, since it often leads to positive reorganization enthalpies, it is a useful starting point. In addition, we believe that the



Scheme 2.

TABLE 1. Reactions used for imposing the restriction for the first guess of the Laidler terms

Reaction A	Reaction B	Fragment(s)
$\text{C}_2\text{H}_6 \rightarrow 2\text{CH}_3$	$\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$	CH_3
$\text{C}_4\text{H}_{10} \rightarrow 2\text{C}_2\text{H}_5$	$\text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5 + \text{H}$	C_2H_5
$\text{C}_6\text{H}_{14} \rightarrow 2i\text{-C}_3\text{H}_7$	$i\text{-C}_3\text{H}_8 \rightarrow i\text{-C}_3\text{H}_7 + \text{H}$	$i\text{-C}_3\text{H}_7$
$(\text{CH}_3)_3\text{CC}(\text{CH}_3)_3 \rightarrow 2\text{C}(\text{CH}_3)_3$	$\text{HC}(\text{CH}_3)_3 \rightarrow \text{C}(\text{CH}_3)_3 + \text{H}$	$t\text{-C}_4\text{H}_9$
$\text{CH}_2\text{CHCHCH}_2 \rightarrow 2\text{C}_2\text{H}_3$	$\text{CH}_2\text{CH}_2 \rightarrow \text{C}_2\text{H}_3 + \text{H}$	C_2H_3
$\text{CH}_2\text{C}(\text{CH}_3)_2 \rightarrow \text{C}_3\text{H}_5 + \text{CH}_3$	$\text{CH}_2\text{CHCH}_3 \rightarrow \text{C}_3\text{H}_5 + \text{H}$	$\text{C}_3\text{H}_5 + \text{CH}_3$
$\text{CHCCCH}_3 \rightarrow \text{C}_2\text{H} + \text{CH}_3$	$\text{CHCH} \rightarrow \text{C}_2\text{H} + \text{H}$	$\text{C}_2\text{H} + \text{CH}_3$

two quantities, bond enthalpy terms and Laidler terms, are related (see Physical Meaning of the Parameters, Sec. 5.3).

The imposed restriction is that the reorganization enthalpy of the methyl fragments in Schemes 1 and 2 will not differ by more than $2 \text{ kJ} \cdot \text{mol}^{-1}$. The value of $2 \text{ kJ} \cdot \text{mol}^{-1}$ was chosen because most of the compounds involved in this first minimization (alkanes, alkenes, and alkynes) had errors associated with the enthalpies of formation that are close to (or less than) that value. This restriction is sensible from a chemical point of view and does not impose any special value on the parameter to be fitted. In the present example, and taking the following enthalpies of formation ($\text{kJ} \cdot \text{mol}^{-1}$); $\Delta_f H^\circ(\text{C}_2\text{H}_6) = -83.8 \pm 0.3$,⁷ $\Delta_f H^\circ(\text{CH}_4) = -74.4 \pm 0.4$,⁷ $\Delta_f H^\circ(\text{CH}_3) = 145.7 \pm 0.8$,¹¹ and $\Delta_f H^\circ(\text{H}) = 217.999 \pm 0.006$,¹¹ $DH^\circ(\text{C-C}) = 375.2 \text{ kJ} \cdot \text{mol}^{-1}$ and $DH^\circ(\text{C-H}) = 438.1 \text{ kJ} \cdot \text{mol}^{-1}$ can be calculated, leading to Eq. (2). Here, $E(\text{C-C}) \equiv \text{C1C1}$ and $E(\text{C-H}) \equiv \text{C0H}$ (the symbols used for all the parameters are given below)

$$\left| (439.3 - \text{C0H}) - \left(\frac{377.6 - \text{C1C1}}{2} \right) \right| \leq 2. \quad (2)$$

Eight different pairs of reactions; involving alkanes, alkenes, and alkynes, imposing eight different restrictions were defined (Table 1).

The result of the first fitting obtained by imposing the restriction above and involving alkanes, alkenes, and alkynes, was a set of Laidler parameters that yield statistical residuals rather close to the desired minimum. In a second step, the restrictions were withdrawn and a new fitting was performed. For compounds from other families (e.g., benzene derivatives) a first fitting of the additional parameters

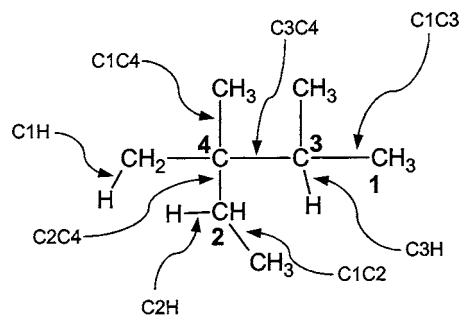


Fig. 1. Four different types of carbon atoms in alkanes (bold) and several C-C and C-H bond types.

TABLE 2. The Laidler parameters for alkanes

C–C bonds	C–H bonds
C1C1, C1C2, C1C3, C1C4	C0H
C2C2, C2C3, C2C4	C1H
C3C3, C3C4	C2H
C4C4	C3H

was made by keeping the values for alkanes, alkenes, and alkynes fixed, leading to a first estimate of the new defined parameters. Then, a second fitting involving all the parameters was performed.

3. Parameters for the Laidler Method

3.1. Alkanes

For the parameterization of the alkanes four different types of carbon atoms were considered: carbon atoms bonded to one, two, three, or four carbons (Fig. 1). Thus, ten different C–C bond types can be defined, from C1C1 to C4C4 (C1C1 being a bond between two type 1 carbons and C4C4 the bond between two type 4 carbon) (see Table 2). For the C–H bonds, the hydrogen atom can be bonded to a carbon that is bonded to zero, one, two, or three carbons (C0H–C3H), leading to four different types of C–H bonds. Therefore, 14 parameters were defined for the alkanes (Table 2). These parameters take into account all the possible combinations of bonds in alkanes. Two of the parameters are only used in one compound: C1C1 in ethane and C0H in methane.

For each compound the enthalpy of formation (gas or condensed phase) or atomization enthalpy is expressed as a sum of the parameters depending on the bond types involved. For example, for 2,3,3-trimethylpentane (Fig. 1) the various quantities can be expressed by a general equation, Eq. (3). For each one of those quantities (gas phase enthalpy of formation, condensed phase enthalpy of formation, and atomization enthalpy) a specific set of parameters was defined.

$$\Delta H = \text{C1C2} + 2\text{C1C3} + 2\text{C1C4} + \text{C2C4} + \text{C3C4} + 15\text{C1H} + 2\text{C2H} + \text{C3H}. \quad (3)$$

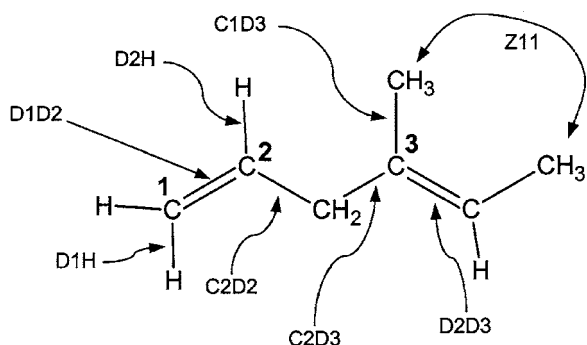


FIG. 2. Three different types of sp^2 carbon atoms in alkenes (bold) and several C–C, C=C, and C–H bond types and steric parameters.

TABLE 3. The Laidler parameters for alkenes

C=C bonds	Single C–C bonds involving an sp^2 carbon	C–H bonds	Spatial parameters (1–4 repulsion)
D1D1, D1D2, D1D3	C1D2, C1D3	D1H	Z11
D2D2, D2D3	C2D2, C2D3	D2H	Z14
D3D3	C3D2, C3D3		Z44
	C4D2, C4D3		

3.2. Alkenes

For the parameterization of alkenes three different types of sp^2 carbon atoms were considered: carbon atoms connected to one, two, or three carbons (Fig. 2). Thus, six distinct C=C double bond types (D1D1–D3D3) and eight C–C single bonds involving an sp^2 carbon (C1D2–C4D3) can be defined (see Table 3 and Fig. 2). For the C–H bonds, the hydrogen atom can be bonded to a carbon only involved in a double bond (D1H) or to a carbon involved in a C–C and a C=C bond (D2H). These parameters, together with those already defined for alkanes, take into account all the possible combinations of bonds in alkenes. However, in some alkenes there are also non-bonded interactions, known as 1,4 interactions, which should be considered. They occur when two groups of atoms exist in the same side of a double bond (Fig. 2). To take this into consideration three extra parameters were considered (Z11, Z14, Z44). At a first glance, it could seem that more parameters would be required to account for all possible situations. However, it is easily concluded that due to the internal rotation of single C–C bonds, the interactions are identical when methyl, ethyl, and isopropyl groups are involved. Only the *tert*-butyl group cannot avoid having a methyl group turned to its neighbor and thus yields a different interaction. Table 4 summarizes the possible non-bonding interactions in alkenes.

3.3. Alkynes

For the parameterization of alkynes it is noted that a sp carbon atom may or may not be bonded to another carbon atom (in addition to the one in the triple bond). Therefore, two different types of carbon atoms should be assumed, lead-

TABLE 4. Non-bonding interactions in alkenes

Group 1	Group 2	Interaction
H	H	
CH ₃	CH ₃	Z11
CH ₃	C ₂ H ₅	Z11
CH ₃	<i>i</i> -C ₃ H ₇	Z11
C ₂ H ₅	C ₂ H ₅	Z11
C ₂ H ₅	<i>i</i> -C ₃ H ₇	Z11
<i>i</i> -C ₃ H ₇	<i>i</i> -C ₃ H ₇	Z11
CH ₃	<i>t</i> -C ₄ H ₉	Z14
C ₂ H ₅	<i>t</i> -C ₄ H ₉	Z14
<i>i</i> -C ₃ H ₇	<i>t</i> -C ₄ H ₉	Z14
<i>t</i> -C ₄ H ₉	<i>t</i> -C ₄ H ₉	Z44

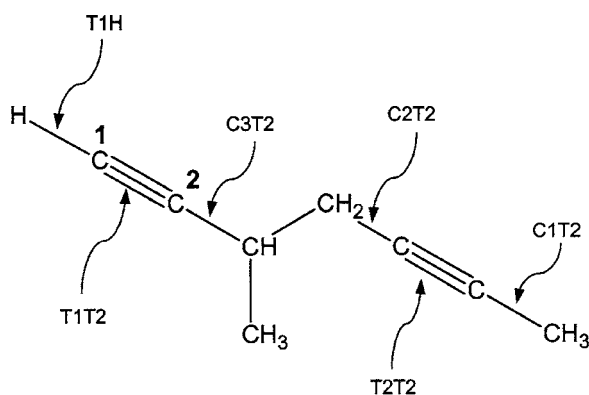


FIG. 3. Two different type of sp carbon atoms (bold) and several C–C, C \equiv C, and C–H bond types.

TABLE 5. The Laidler parameters for alkynes

C \equiv C bonds	Single C–C bonds involving an sp carbon	C–C bonds
T1T1	C1T2	T1H
T1T2	C2T2	
T2T2	C3T2	
	C4T2	

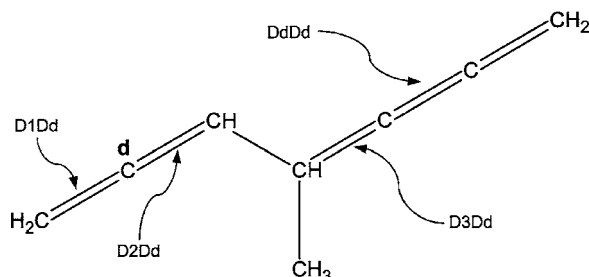


FIG. 4. New type of carbon in allenes (bold) and the new C=C bond types.

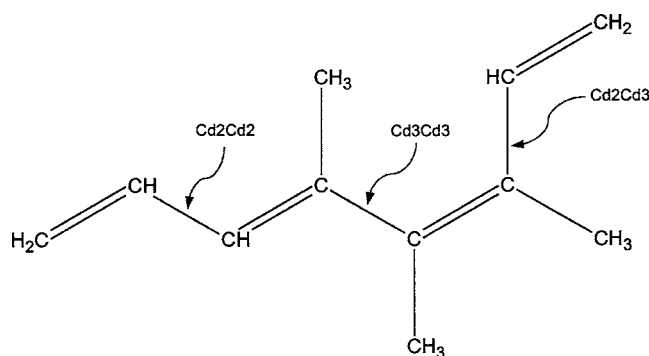


FIG. 5. Three new bond types in conjugated polyenes.

TABLE 6. Additional Laidler parameters for allenes, dienes, and polyenes

C=C bonds	C–C bonds between two C=C bonds
D1Dd	Cd2Cd2
D2Dd	Cd2Cd3
D3Dd	Cd3Cd3
DdDd	

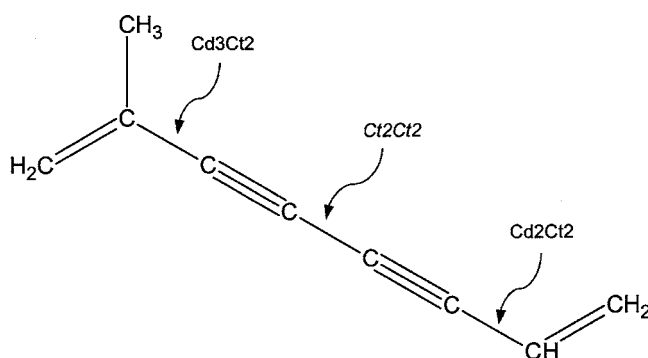


FIG. 6. Three different types of bonds in diynes and alkyne-enes.

ing to three C \equiv C bonds (T1T1, T1T2, and T2T2) and four C–C bonds involving an sp carbon (C1T2–C4T2) (Fig. 3 and Table 5). For the C–H bonds only one parameter, T1H, is required. These eight parameters, together with those defined for alkanes and alkenes, take into account all the possible additional combinations of bonds in alkynes.

3.4. Allenes, Dienes, and Polyenes

For the parameterization of allenes the only new type of carbon is the one that sits in the middle of two double bonds. As observed in Fig. 4, this leads to four new types of bonds.

In the case of polyenes new parameters will be necessary only in the case of conjugated double bonds. As shown in Fig. 5, three new types of bonds occur inbetween two double bonds, depending on the number of carbons bonded to the carbons involved in the bond (two or three). All these additional parameters for allenes, dienes, and polyenes are compiled in Table 6.

3.5. Diynes and Alkyne-enes

For the parameterization of diynes and alkyne-enes some additional parameters are necessary (Fig. 6 and Table 7). Only one possibility exists for a single bond between two triple bonds (Ct2Ct2) but two cases are possible when the neighbors are a triple and a double bond (Cd2Ct2 and Cd3Cd2).

3.6. Cycloalkanes and Cycloalkenes

The bonds parameters needed to apply the method to cycloalkanes and cycloalkenes are already described. However, these compounds will have a ring strain due to the energy spent in bending the compound to close the cycle. Eight parameters (ZS3–ZS10) were defined to take into account

TABLE 7. Additional Laidler parameters for diynes and alkyne-enes

C–C bonds between C=C and C \equiv C bonds	C–C bonds between two C \equiv C bonds
Cd2Ct2	Ct2Ct2
Cd3Cd2	

TABLE 8. Additional Laidler parameters for radicals

Original parameter	Parameters for carbon radicals
C0H	C0R
C1H	C1R
C2H	C2R
C3H	C3R

the strain in cycloalkanes, referring to the number in the parameter to the number of atoms in the ring. In the same way five parameters (ZD4–ZD8) were defined for cycloalkenes.

3.7. Alkyl Radicals

The Laidler scheme can also be applied to estimate enthalpies of formation and atomization enthalpies of radicals in the gas phase. An alkyl radical is a molecule where one C–H bond suffers a homoleptic cleavage leaving one unpaired electron on the carbon atom. The simplest approach for parameterization is keeping the set of parameters derived above and defining new parameters only for these new conceptual bonds between a carbon atom and an unpaired electron. For instance, in the case of a propyl radical, one of the C–H bond parameters (C0H) will be replaced by a new parameter (C0R). Since four types of carbon atoms can be considered, four new parameters will be defined (Table 8).

3.8. Benzene Derivatives

For benzene and its derivatives some new parameters must be defined since an aromatic bond cannot be described by the parameters proposed so far. A carbon atom from a benzenic ring can be bonded to two other ring carbons and a hydrogen or to the ring carbons and another carbon atom. This defines three different types of bonds in the ring: A2A2, A2A3, and A3A3 (Fig. 7).

Also, one parameter is needed for the aromatic carbon–hydrogen bond (A2H) and four different parameters can be defined for the bond between a benzene ring carbon and a carbon from an alkyl group, depending on the number of carbons bonded to the sp^3 carbon: C1A3, C2A3, C3A3, and C4A3. For non-alkane substituents (with double and triple bonds), three new parameters must be defined (Fig. 8 and Table 9).

As considered for alkenes, some non-bonding interactions must be considered for *ortho*-substituents. We have designated these terms as ZA11, ZA14, and ZA44. The meaning of these parameters is similar to the one described for alkenes. The number 1 applies to methyl, ethyl, or isopropyl groups (primary, secondary, and tertiary carbons) and the number 4 applies to quaternary carbon substituents. When more than two substituents are present in adjacent positions, the internal rotation of some of them can be severely hindered and more terms are required (ZA1'1, ZA1'4, ZA1'1', ZA1'4', ZA4'1, and ZA4'4'), leading to a total

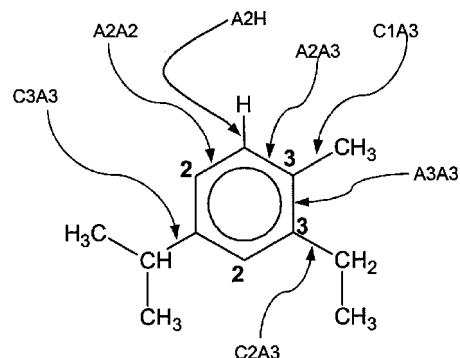


FIG. 7. Two different type of carbons in a benzenic ring (bold) and several carbon–carbon and carbon–hydrogen bond types.

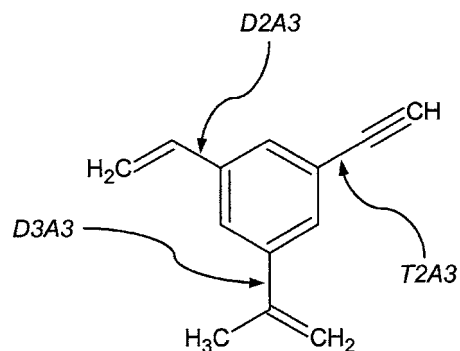


FIG. 8. Additional bond types between an aromatic ring and unsaturated substituents.

TABLE 9. Additional Laidler parameters for benzenic compounds

Bonds in benzenic ring	Alkyl groups bonded to the aromatic ring	Non-alkyl groups bonded to the aromatic ring	Spatial parameters (neighbors repulsion)		
A2A2	C1A3	D2A3	ZA11	ZA11'	ZA1'4'
A2A3	C2A3	D3A3	ZA14	ZA1'4	ZA4'1
A3A3	C3A3	T2A3	ZA44	ZA1'1'	ZA4'4'
A2H	C4A3				

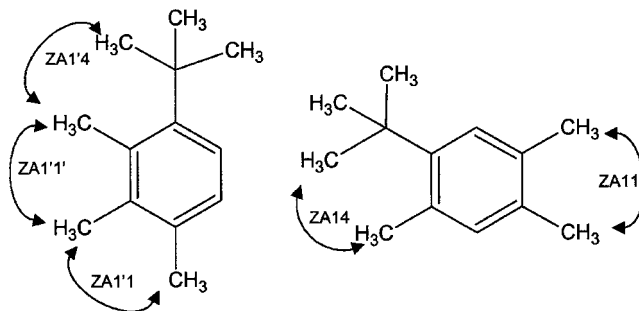


FIG. 9. Non-bonding interactions in benzenic rings.

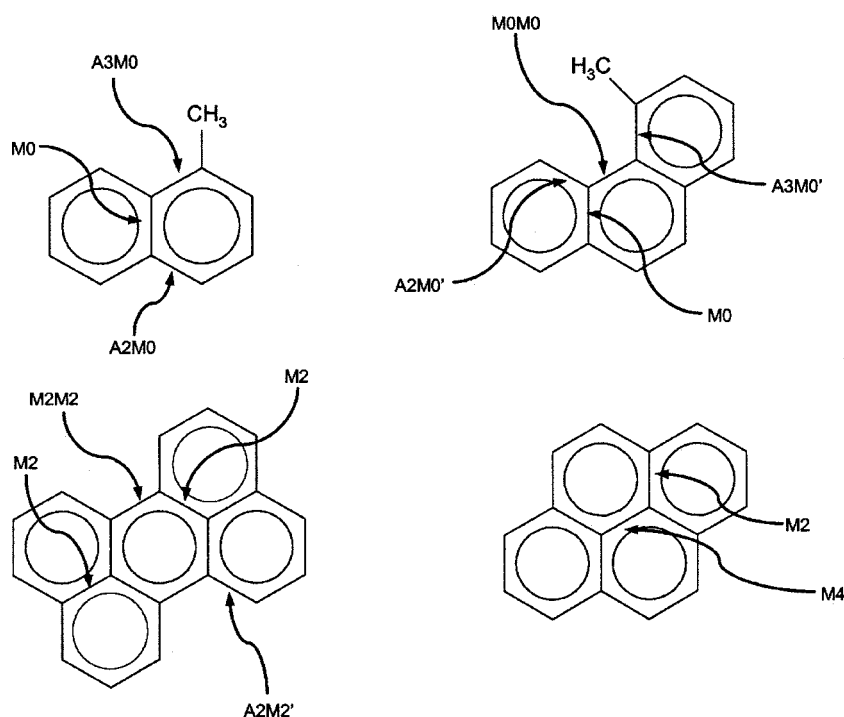


FIG. 10. Three different types of shared bonds in polyaromatic hydrocarbons (M0, M2, and M4) and several new bond types.

of nine different non-bonding interactions in benzene rings (Fig. 9 and Table 9). The number identified with a prime refers to a substituent in between two other substituents.

3.9. Biphenyls

The only not yet defined parameter for biphenyls is the one related to the bond between the two aromatic rings. Thus, a new parameter was defined for this type of bond as Ca3a3.

3.10. Polyaromatic Hydrocarbons

The terms defined for benzene derivatives are not enough to describe polyaromatic hydrocarbons. These molecules, which are characterized by two or more fused benzene rings, require several new types of parameters. Three types of shared bonds can be defined: shared bond connected to zero, two, or four other shared bonds (M0, M2, and M4). In addition, it will be necessary to define non-shared bonds connecting two shared ones (M0M0, M0M2, and M2M2), bonds connecting aromatic carbons to shared bonds (A2M0, A2M2, A3M0, and A3M2), and bonds connecting aromatic carbons to shared bonds and MXMX bonds (X=0 and 2) (A2M0', A2M2', A3M0', and A3M2') (Fig. 10 and Table 10).

4. Experimental Values

As the proposed method is empirical, relying on a fitting procedure, the quality of the experimental database is crucial, i.e., the input values should be accurate and thermochemically consistent. By thermochemical consistency it is meant that all the values for the standard enthalpies of formation calculated from experimental values of reaction or

combustion enthalpies rely on a single set of auxiliary data. For instance, suppose that the reported enthalpies of formation of compounds A and B, both obtained from highly accurate measurements of their combustion enthalpies, were reported by two different groups who had different choices for the values of the standard enthalpies of formation of water and carbon dioxide. In this case, the reported $\Delta_f H^\circ(A)$ will be "inconsistent" with $\Delta_f H^\circ(B)$. Although in the case of hydrocarbons this is not a serious problem, because $\Delta_f H^\circ(H_2O, g)$ and $\Delta_f H^\circ(CO_2, g)$ are well established, inconsistency may reveal when A and B have large numbers of carbon atoms and/or when the original literature reference is very old. It is therefore important to calculate, or recalculate, all values using the same set of auxiliary data values in order to ensure consistency. In Table 11 the values of the standard enthalpies of formation were taken from the compilation made by Pedley,⁷ unless noted otherwise. When taken from other sources the values were checked to see if they rely on the same set of auxiliary data as Pedley's. If not, they were recalculated in order to be consistent. The atomization enthalpies were derived by using $\Delta_f H^\circ(H, g) = 217.999 \pm 0.006 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta_f H^\circ(C, g) = 716.67 \pm 0.46 \text{ kJ} \cdot \text{mol}^{-1}$.¹¹

For the radicals the values were taken from Simões and

TABLE 10. Additional Laidler parameters for polyaromatic hydrocarbons

Merged bonds	Non-merged bonds between two shared bonds	Aromatic bonds connected to shared bonds	
M0	M0M0	A2M0	A3M0
M2	M0M2	A2M0'	A3M0'
M4	M2M2	A2M2	A3M2
		A2M2'	A3M2'

TABLE 11. Experimental and estimated values for hydrocarbons (data in $\text{kJ}\cdot\text{mol}^{-1}$)

Compound		Experimental gas-phase enthalpy of formation ^a		Estimated value and difference between exp. and fitted gas-phase enthalpy of formation		Experimental condensed-phase enthalpy of formation ^a		Estimated value and difference between exp. and fitted condensed phase enthalpy of formation		Atomization enthalpy ^b		Estimated value and difference between exp. and fitted atomization enthalpy	
		Value	Error	Value	Diff.	Value	Error	Value	Diff.	Value	Error	Value	Diff.
alkanes													
CH ₄	methane	-74.4	0.4	-74.4	0.0					1663.1	0.4	1663.1	0.0
C ₂ H ₆	ethane	-83.8	0.3	-82.8	1.0	-93.6	2.5	-93.6	0.0	2825.1	0.3	2824.1	1.0
C ₃ H ₈	propane	-104.7	0.5	-104.8	0.1	-120.9	2.5	-122.2	1.3	3998.7	0.5	3998.9	0.2
C ₄ H ₁₀	butane	-125.7	0.6	-125.5	0.2	-147.3	2.5	-147.6	0.3	5172.4	0.6	5172.2	0.2
	isobutane	-134.2	0.6	-134.1	0.1	-154.2	1.2	-154.4	0.2	5180.9	0.6	5180.8	0.1
C ₅ H ₁₂	pentane	-146.9	0.8	-146.2	0.7	-173.5	0.7	-173.0	0.5	6346.2	0.8	6345.5	0.7
	butane, 2-methyl	-153.6	0.9	-152.9	0.7	-178.4	0.9	-178.1	0.3	6352.9	0.9	6352.3	0.7
C ₆ H ₁₄	propane, 2,2-dimethyl	-168.0	0.8	-167.8	0.2	-190.2	0.7	-189.8	0.4	6367.3	0.8	6367.2	0.1
	hexane	-166.9	0.8	-166.9	0.0	-198.7	0.8	-198.4	0.3	7518.9	0.8	7518.8	0.1
C ₇ H ₁₆	pentane, 2-methyl	-174.6	0.9	-173.6	1.0	-204.6	0.9	-203.5	1.1	7526.6	0.9	7525.6	1.0
	pentane, 3-methyl	-171.9	0.9	-171.6	0.3	-202.4	0.9	-201.7	0.7	7523.9	0.9	7523.7	0.2
	butane, 2,2-dimethyl	-185.9	0.9	-183.9	2.0	-213.8	0.9	-211.3	2.5	7537.9	0.9	7535.9	2.0
	butane, 2,3-dimethyl	-178.1	0.9	-176.0	2.1	-207.4	0.9	-205.1	2.3	7530.1	0.9	7528.0	2.1
	heptane	-187.6	1.3	-187.6	0.0	-224.2	1.3	-223.8	0.4	8692.3	1.3	8692.2	0.1
	hexane, 2-methyl	-194.5	1.0	-194.3	0.2	-229.5	1.0	-228.9	0.6	8699.2	1.0	8698.9	0.3
C ₈ H ₁₈	hexane, 3-methyl	-191.3	1.9	-192.3	1.0	-226.4	1.9	-227.1	0.7	8696.0	1.9	8697.0	1.1
	pentane, 3-ethyl	-189.5	1.0	-190.4	0.9	-224.9	1.0	-225.4	0.5	8694.2	1.0	8695.1	1.0
	pentane, 2,2-dimethyl	-205.7	1.5	-204.6	1.1	-238.3	1.5	-236.7	1.6	8710.4	1.5	8709.2	1.1
	pentane, 2,3-dimethyl	-198.7	1.4	-194.7	4.0	-233.1	1.4	-228.8	4.3	8703.4	1.4	8699.4	4.0
	pentane, 2,4-dimethyl	-201.6	1.1	-201.0	0.6	-234.6	1.1	-234.0	0.6	8706.3	1.1	8705.7	0.6
	pentane, 3,3-dimethyl	-201.0	1.1	-199.9	1.1	-234.2	1.1	-232.9	1.3	8705.7	1.1	8704.6	1.1
	butane, 2,2,3-trimethyl	-204.4	1.3	-201.9	2.5	-236.5	1.3	-233.9	2.6	8709.1	1.3	8706.6	2.5
	octane	-208.5	1.3	-208.3	0.2	-250.1	1.3	-249.2	0.9	9865.8	1.3	9865.5	0.3
	heptane, 2-methyl	-215.3	1.4	-215.0	0.3	-255.0	1.4	-254.3	0.7	9872.6	1.4	9872.2	0.4
	heptane, 3-methyl	-212.5	1.3	-213.1	0.6	-252.3	1.3	-252.5	0.2	9869.8	1.3	9870.4	0.5
	heptane, 4-methyl	-211.9	1.3	-213.1	1.2	-251.6	1.3	-252.5	0.9	9869.2	1.3	9870.4	1.1
	hexane, 3-ethyl	-210.7	1.3	-211.1	0.4	-250.4	1.3	-250.8	0.4	9868.0	1.3	9868.5	0.4
	hexane, 2,2-dimethyl	-224.5	1.3	-225.3	0.8	-261.9	1.3	-262.1	0.2	9881.8	1.3	9882.6	0.7
	hexane, 2,3-dimethyl	-213.8	1.6	-215.4	1.6	-252.6	1.6	-254.2	1.6	9871.1	1.6	9872.8	1.6
	hexane, 2,4-dimethyl	-219.2	1.3	-219.7	0.5	-257.0	1.3	-257.6	0.6	9876.5	1.3	9877.1	0.6
	hexane, 2,5-dimethyl	-222.5	1.6	-221.7	0.8	-260.4	1.6	-259.4	1.0	9879.8	1.6	9879.0	0.9
	hexane, 3,3-dimethyl	-219.9	1.3	-220.6	0.7	-257.5	1.3	-257.5	0.0	9877.2	1.3	9877.9	0.7
	hexane, 3,4-dimethyl	-212.8	1.6	-213.5	0.7	-251.8	1.6	-252.4	0.6	9870.1	1.6	9870.9	0.7
	pentane, 3-ethyl, 2-methyl	-211.0	1.4	-213.5	2.5	-249.6	1.4	-252.4	2.8	9868.3	1.4	9870.9	2.5
	pentane, 3-ethyl, 3-methyl	-214.8	1.4	-215.9	1.1	-252.8	1.4	-254.4	1.6	9872.1	1.4	9873.3	1.2
	pentane, 2,2,3-trimethyl	-219.9	1.6	-220.7	0.8	-256.9	1.6	-257.5	0.6	9877.2	1.6	9878.0	0.8
	pentane, 2,2,4-trimethyl	-223.9	1.5	-232.0	8.1	-259.2	1.5	-267.2	8.0	9881.2	1.5	9889.3	8.1
	pentane, 2,3,3-trimethyl	-216.2	1.5	-217.9	1.7	-253.5	1.5	-255.5	2.0	9873.5	1.5	9875.3	1.7
	pentane, 2,3,4-trimethyl	-217.2	1.7	-217.8	0.6	-255.0	1.7	-255.8	0.8	9874.5	1.7	9875.1	0.6
	butane, 2,2,3,3-tetramethyl	-226.0	1.4	-226.0	0.0	-269.0	1.4	-269.0	0.0	9883.3	1.4	9883.3	0.0
alkenes													
C ₂ H ₄	ethene	52.5	0.3	52.5	0.0					2252.8	0.3	2252.8	0.0
C ₃ H ₆	propene	20.0	0.7	19.8	0.2	4.0	2.5	2.8	1.2	3438.0	0.7	3437.7	0.3
C ₄ H ₈	1-butene	0.1	0.9	0.1	0.0	-20.8	1.0	-20.8	0.0	4610.6	0.9	4610.6	0.0
	(Z)-2-butene	-7.1	1.0	-8.6	1.5	-29.8	1.0	-30.9	1.1	4617.8	1.0	4619.1	1.3
C ₅ H ₁₀	(E)-2-butene	-11.4	1.0	-12.4	1.0	-33.3	1.1	-34.3	1.0	4622.1	1.0	4622.8	0.7
	propene, 2-methyl	-16.9	0.9	-17.7	0.8	-37.5	0.9	-39.0	1.5	4627.6	0.9	4628.8	1.2
	1-pentene	-21.1	0.9	-20.8	0.3	-46.9	0.7	-47.2	0.3	5784.4	0.9	5784.1	0.3
	(Z)-2-pentene	-27.6	0.9	-28.6	1.0	-53.7	0.7	-55.5	1.8	5790.9	0.9	5792.2	1.3
	(E)-2-pentene	-31.9	1.0	-32.3	0.4	-58.2	0.8	-58.9	0.7	5795.2	1.0	5795.8	0.6
	1-butene, 2-methyl	-35.2	0.9	-36.5	1.3	-61.1	0.8	-62.3	1.2	5798.5	0.9	5799.9	1.3
C ₆ H ₁₂	1-butene, 3-methyl	-27.5	0.7	-28.4	0.9	-51.5	0.6	-53.0	1.5	5790.8	0.7	5791.8	1.0
	2-butene, 2-methyl	-41.7	1.0	-42.8	1.1	-68.6	1.1	-69.3	0.7	5805.0	1.0	5805.5	0.5
	1-hexene	-43.5	1.6	-41.5	2.0	-74.2	1.6	-72.6	1.6	6959.5	1.6	6957.4	2.1
	(Z)-2-hexene	-52.3	1.3	-49.3	3.0	-83.9	1.3	-80.9	3.0	6968.3	1.3	6965.5	2.8
	(E)-2-hexene	-53.9	1.5	-53.0	0.9	-85.5	1.5	-84.3	1.2	6969.9	1.5	6969.2	0.7
	(Z)-3-hexene	-47.6	1.3	-48.5	0.9	-78.9	1.3	-80.1	1.2	6963.6	1.3	6965.3	1.7

TABLE 11. Experimental and estimated values for hydrocarbons (data in $\text{kJ}\cdot\text{mol}^{-1}$)—Continued

		Experimental gas-phase enthalpy of formation ^a		Estimated value and difference between exp. and fitted gas-phase enthalpy of formation		Experimental condensed-phase enthalpy of formation ^a		Estimated value and difference between exp. and fitted condensed phase enthalpy of formation		Atomization enthalpy ^b		Estimated value and difference between exp. and fitted atomization enthalpy	
Compound		Value	Error	Value	Diff.	Value	Error	Value	Diff.	Value	Error	Value	Diff.
C ₇ H ₁₄	(E)-3-hexene	−54.4	1.3	−52.3	2.1	−86.1	1.3	−83.5	2.6	6970.4	1.3	6968.9	1.5
	1-pentene, 2-methyl	−59.4	1.3	−57.2	2.2	−90.0	1.3	−87.7	2.3	6975.4	1.3	6973.2	2.2
	1-pentene, 3-methyl	−49.5	1.5	−47.2	2.3	−78.2	1.5	−76.6	1.6	6965.5	1.5	6963.2	2.3
	1-pentene, 4-methyl	−51.3	1.8	−48.2	3.1	−80.0	1.8	−77.7	2.3	6967.3	1.8	6964.2	3.1
	2-pentene, 2-methyl	−66.9	1.4	−62.7	4.2	−98.5	1.4	−93.9	4.6	6982.9	1.4	6978.6	4.3
	(Z)-2-pentene, 3-methyl	−62.3	1.4	−61.6	0.7	−94.5	1.4	−92.6	1.9	6978.3	1.4	6976.6	1.7
	(E)-2-pentene, 3-methyl	−63.1	1.3	−61.6	1.5	−94.6	1.3	−92.6	2.0	6979.1	1.3	6976.6	2.5
	(Z)-2-pentene, 4-methyl	−57.5	1.1	−56.9	0.6	−87.0	1.1	−86.6	0.4	6973.5	1.1	6973.2	0.3
	(E)-2-pentene, 4-methyl	−61.5	1.4	−60.6	0.9	−91.6	1.4	−90.1	1.5	6977.5	1.4	6976.9	0.7
	1-butene, 2-ethyl	−56.0	1.4	−55.3	0.7	−87.1	1.4	−85.6	1.5	6972.0	1.4	6970.9	1.1
	1-butene, 2,3-dimethyl	−62.4	1.3	−61.6	0.8	−93.2	1.9	−92.0	1.2	6978.4	1.3	6977.7	0.7
	1-butene, 3,3-dimethyl	−60.3	1.2	−57.3	3.0	−87.5	1.3	−84.5	3.0	6976.3	1.2	6973.1	3.2
	2-butene, 2,3-dimethyl	−68.1	1.1	−68.1	0.0	−101.4	1.3	−101.4	0.0	6984.1	1.1	6984.1	0.0
	1-heptene	−62.3	0.9	−62.3	0.0	−97.9	0.9	−98.0	0.1	8131.0	0.9	8130.8	0.2
	(Z)-2-heptene			−70.0		−105.1	0.8	−106.3	1.2			8138.9	
	(E)-2-heptene			−73.8		−109.5	0.8	−109.7	0.2			8142.5	
	(Z)-3-heptene			−76.9		−104.3	0.7	−105.1	0.8			8489.8	
	(E)-3-heptene			−80.6		−109.3	1.0	−108.5	0.8			8493.5	
	1-hexene, 5-methyl	−65.7	1.0	−68.9	3.2	−100.0	0.6	−103.1	3.1	8134.4	1.0	8137.5	3.1
	(Z)-3-hexene, 3-methyl	−79.4	1.1	−81.5	2.1	−115.9	1.1	−117.2	1.3	8148.1	1.1	8149.7	1.6
	(E)-3-hexene, 3-methyl	−76.8	1.1	−81.5	4.7	−112.7	1.1	−117.2	4.5	8145.5	1.1	8149.7	4.2
	1-pentene, 2,4-dimethyl	−83.8	1.3	−84.6	0.8	−117.0	1.3	−118.2	1.2	8152.5	1.3	8153.2	0.8
	1-pentene, 4,4-dimethyl	−81.6	1.9	−79.2	2.4	−110.6	1.8	−110.9	0.3	8150.3	1.9	8147.8	2.4
	(Z)-2-pentene, 4,4-dimethyl	−72.6	1.4	−72.6	0.0	−105.3	1.4	−105.3	0.0	8141.3	1.4	8141.3	0.0
	(E)-2-pentene, 4,4-dimethyl	−88.8	1.1	−89.5	0.7	−121.7	1.1	−121.7	0.0	8157.5	1.1	8158.1	0.6
	2-pentene, 2,4-dimethyl	−88.7	1.1	−91.1	2.4	−123.1	1.1	−125.1	2.0	8157.4	1.1	8159.6	2.2
	1-butene, 2-ethyl, 3-methyl	−79.5	1.4	−80.3	0.8	−114.1	1.4	−115.3	1.2	8148.2	1.4	8148.8	0.7
	1-butene, 2,3,3-trimethyl	−85.5	1.3	−85.5	0.0	−117.7	1.3	−117.7	0.0	8154.2	1.3	8154.2	0.0
C ₁₀ H ₂₀	(Z)-3-hexene, 2,2,5,5-tetramethyl	−127.0		−127.0	0.0	−163.6	1.9	−163.6	0.0	11653.7		11653.7	0.0
	(E)-3-hexene, 2,2,5,5-tetramethyl	−165.5	2.6	−166.6	1.1	−207.5	2.6	−209.0	1.5	11692.2	2.6	11693.5	1.3
alkynes													
C ₂ H ₂	ethyne	226.7	0.8	226.7	0.0	208.7 ^d	5	208.7	0.0	1642.6	0.8	1642.6	0.0
C ₃ H ₄	propyne	185.4	0.9	186.3	0.9			165.5		2836.6	0.9	2835.8	0.8
C ₄ H ₆	1-butyne	165.2	0.9	164.7	0.5	141.4	1.3	140.1	1.3	4009.5	0.9	4010.0	0.6
	2-butyne	145.1	1.0	147.4	2.3	119.1	1.1	119.7	0.6	4029.6	1.0	4027.3	2.3
C ₅ H ₈	1-pentyne	144.3	2.1	144.0	0.3			114.7		5183.0	2.1	5183.4	0.3
	2-pentyne	128.9	2.1	125.9	3.0			94.4		5198.4	2.1	5201.5	3.1
	1-butyne, 3-methyl	136.4	2.1	136.4	0.0	109.1 ^d	5	109.1	0.0	5190.9	2.1	5191.0	0.0
C ₆ H ₁₀	1-hexyne	122.3	1.2	123.3	1.0			89.3		6357.7	1.2	6356.7	1.0
	2-hexyne	107.7	2.4	105.2	2.5			69.0		6372.3	2.4	6374.9	2.6
	3-hexyne	105.4	1.9	104.3	1.1			69.0		6374.6	1.9	6375.8	1.2
	1-butyne, 3,3-dimethyl	107.0	1.3	107.0	0.0	77.9 ^c	1.5	77.9	0.0	6373.0	1.3	6373.0	0.0
C ₇ H ₁₂	1-heptyne	103.8	2.6	102.6	1.2	62.8 ^c	0	63.9	1.1	7528.9	2.6	7530.0	1.2
	2-heptyne	84.8	2.2	84.4	0.4			43.6		7547.9	2.2	7548.2	0.3
	3-heptyne	82.8	2.4	83.6	0.8			43.6		7549.9	2.4	7549.1	0.7
C ₈ H ₁₄	1-octyne	80.7	3.6	81.9	1.2	38.4 ^d	3.6	38.5	0.1	8704.6	3.6	8703.4	1.3
	2-octyne	63.8	1.5	63.7	0.1	19.3 ^d	1.5	18.2	1.1	8721.5	1.5	8721.5	0.0
	3-octyne	62.5	1.8	62.9	0.4	18.6 ^d	1.8	18.2	0.4	8722.8	1.8	8722.5	0.4
	4-octyne	60.1	2.1	62.9	2.8	17.3 ^d	2.1	18.2	0.9	8725.2	2.1	8722.5	2.8
C ₉ H ₁₆	1-nonyne	62.3	3.0	61.2	1.1			13.1		9875.7	3.0	9876.7	1.0
	2-nonyne	42.6	3.0	43.0	0.4			−7.3		9895.4	3.0	9894.9	0.6
	3-nonyne	42.0	2.5	42.2	0.2			−7.2		9896.0	2.5	9895.8	0.2
	4-nonyne	42.0	2.8	42.2	0.2			−7.2		9896.0	2.8	9895.8	0.2
allenes, dienes and poly-enes													
C ₃ H ₄	propadiene	190.5	1.1	190.3	0.2			38.5		2831.5	1.1	2831.6	0.0
C ₄ H ₆	1,2-butadiene	162.3	0.6	161.6	0.7	139.0	0.6	139.0	0.0	4012.4	0.6	4012.9	0.5
	1,3-butadiene	110.0	1.1	108.8	1.2	88.5	1.2	88.5	0.0	4064.7	1.1	4065.8	1.1
C ₅ H ₈	1,2-pentadiene	140.7	0.7	141.7	1.0			114.4		5186.6	0.7	5186.0	0.6

TABLE 11. Experimental and estimated values for hydrocarbons (data in kJ·mol⁻¹)—Continued

		Experimental gas-phase enthalpy of formation ^a		Estimated value and difference between exp. and fitted gas-phase enthalpy of formation		Experimental condensed-phase enthalpy of formation ^a		Estimated value and difference between exp. and fitted condensed phase enthalpy of formation		Atomization enthalpy ^b		Estimated value and difference between exp. and fitted atomization enthalpy	
Compound		Value	Error	Value	Diff.	Value	Error	Value	Diff.	Value	Error	Value	Diff.
C ₆ H ₁₀	(Z)-1,3-pentadiene	81.4	1.2	80.3	1.1			54.8		5245.9	1.2	5247.2	1.3
	(E)-1,3-pentadiene	76.1	0.8	76.6	0.5			51.4		5251.2	0.8	5250.9	0.4
	1,4-pentadiene	105.7	1.1	104.5	1.2			78.6		5221.6	1.1	5222.7	1.1
	2,3-pentadiene	133.1	0.8	132.9	0.2			239.5		5194.2	0.8	5194.3	0.0
	1,2-butadiene, 3-methyl	129.1 ^c	0.6	129.1	0.0	101.2	0.5	101.2	0.0	5198.3	0.6	5198.3	0.0
	1,3-butadiene, 2-methyl	75.5	1.1	75.5	0.0	48.2	1.3	48.2	0.0	5251.8	1.1	5251.8	0.0
	1,5-hexadiene	84.2	0.9	83.8	0.4	54.1	0.4	53.2	0.0	6395.8	0.9	6396.0	0.2
	(Z)-1,3-hexadiene	59.0 ^c	2.0	60.4	1.4			30.2		6421.0	2.0	6420.3	0.7
	(E)-1,3-hexadiene	54.0 ^c	2.0	56.7	2.7			26.8		6426.0	2.0	6423.9	0.0
	(Z)-1,4-hexadiene	77.0 ^c	2.0	76.1	0.9			44.9		6403.0	2.0	6404.1	0.0
	(E)-1,4-hexadiene	74.0 ^c	2.0	72.3	1.7			41.4		6406.0	2.0	6407.8	1.7
	(Z,Z)-2,4-hexadiene	52.0 ^c	2.0	51.9	0.1			21.2		6428.0	2.0	6428.6	0.6
	(E,Z)-2,4-hexadiene	48.0 ^c	2.0	48.1	0.1			17.7		6432.0	2.0	6432.3	0.3
	(E,E)-2,4-hexadiene	44.0 ^c	2.0	44.4	0.4			14.3		6436.0	2.0	6435.9	0.1
1,3-butadiene, 2,3-dimethyl	45.3	1.1	45.3	0.0	14.4	1.2	14.4	0.0	6434.7	1.1	6434.7	0.0	
diynes and alkyne-enes													
C ₄ H ₄	1-buten-3-yne	295.0 ^c		290.9	4.1					3443.7		3447.6	4.0
C ₅ H ₆	(Z)-3-penten-1-yne	258.0 ^c		262.4	4.4	226.5	4.6	229.1	2.6	4633.3		4629.0	4.3
	(E)-3-penten-1-yne	259.0 ^c		258.7	0.0	228.2	1.8	225.6	0.0	4632.3		4632.7	0.0
C ₆ H ₆	1-buten-3-yne, 2-methyl	259.0 ^c		259.0	0.0	231.0 ^c	0.8	231.0	0.0	4632.3		4632.3	0.0
	1,5-hexadiyne			413.5		384.2	4.2	377.1	7.1			5194.6	
	2,4-hexadiyne	377.4 ^c		377.4	0.0	335.2 ^c	5.0	335.2	0.0	5230.6		5230.6	0.0
cycloalkanes													
C ₃ H ₆	cyclopropane	53.3	0.5	49.4	3.9	35.2	2.5	30.9	4.3	3404.7	0.5	3408.6	3.9
C ₄ H ₈	cyclobutane	27.7	1.1	27.7	0.0	3.7	0.5	3.7	0.0	4583.0	1.1	4583.0	0.0
C ₅ H ₁₀	cyclopropane, 1-1 dimethyl	−8.2	1.1	−4.3	3.9	−33.3	0.7	−29.0	4.3	5771.5	1.1	5767.7	3.9
	cyclopentane	−76.4	0.7	−78.6	2.2	−105.1	0.7	−107.1	2.0	5839.7	0.7	5841.9	2.1
C ₆ H ₁₂	cyclopentane, methyl	−106.2	0.7	−104.0	2.2	−137.9	0.7	−135.9	2.0	7022.2	0.7	7020.1	2.1
	cyclohexane	−123.3	0.8	−126.6	3.3	−156.4	0.8	−159.2	2.8	7039.3	0.8	7042.5	3.2
C ₇ H ₁₄	cyclohexane, methyl	−154.6	1.0	−152.0	2.6	−190.1	1.0	−187.9	2.2	8223.3	1.0	8220.7	2.6
	cycloheptane	−118.1	0.9	−118.1	0.0	−156.6	0.9	−156.6	0.0	8186.8	0.9	8186.8	0.0
C ₈ H ₁₆	cyclohexane, ethyl	−171.5	1.5	−170.8	0.7	−212.1	1.5	−211.5	0.6	9392.8	1.5	9392.2	0.7
	cyclooctane	−124.4	1.0	−124.4	0.0	−167.7	1.0	−167.7	0.0	9345.7	1.0	9345.7	0.0
C ₉ H ₁₈	cyclononane	−132.8	1.5	−132.8	0.0	−181.2	1.0	−181.2	0.0	10506.8	1.5	10506.8	0.0
C ₁₀ H ₂₀	cyclodecane	−154.3	1.5	−154.3	0.0	−206.7	0.9	−206.7	0.0	11681.0	1.5	11681.0	0.0
cycloalkenes													
C ₄ H ₆	cyclobutene	156.7	1.5	156.7	0.0					4018.0	1.5	4017.9	0.0
C ₅ H ₆	1,3-cyclopentadiene	134.3	1.5	131.5	2.8	105.9	1.5	103.4	2.5	4757.0	1.5	4760.6	3.6
C ₅ H ₈	cyclopentene	34.0	1.4	33.3	0.7	4.3 ^c	0.8	4.0	0.3	5293.3	1.4	5294.1	0.8
C ₆ H ₁₀	cyclopentene, 1-methyl	−3.6 ^c	0.8	0.3	3.9	−36.4 ^c	0.6	−33.1	3.3	6483.6	0.8	6478.5	5.1
	cyclopentene, 3-methyl	7.4 ^c	0.7	6.9	0.5	−24.9 ^c	1.8	−25.4	0.5	6472.6	0.7	6473.3	0.6
C ₇ H ₁₂	cyclohexene	−4.3 ^c	1.0	−4.3	0.0	−37.8	8.2	−34.2	3.6	6484.3	1.0	6490.7	6.4
	cyclohexene, 1-methyl	−43.3	0.7	−43.3	0.0	−81.2	0.7	−84.5	3.3	7676.0	0.7	7669.2	6.8
	cycloheptene	−9.2	1.1	−9.2	0.0					7641.9	1.1	7641.8	0.1
C ₈ H ₁₄	cyclooctene	−27.0	1.2	−27.0	0.0	−74.0	1.9	−74.0	0.0	8812.3	1.2	8812.3	0.1
alkyl radicals													
CH ₃	methyl	146.9 ^c	0.6	146.9	0.0								
C ₂ H ₅	ethyl	119.0 ^c	4.0	118.0	1.0								
C ₃ H ₇	propyl	96.0 ^c	4.0	96.1	0.1								
	i-propyl	84.0 ^c	8.0	83.4	0.6								
C ₄ H ₉	butyl	74.0 ^c	8.0	75.4	1.4								
	s-butyl	62.0 ^c	8.0	62.6	0.6								
	i-butyl	68.0 ^c	8.0	66.8	1.2								
	t-butyl	44.0 ^c	6.0	44.0	0.0								
C ₅ H ₁₁	pentyl	54.0 ^c	8.0	54.7	0.7								
	propyl, 2,2-dimethyl	33.0 ^c	10.0	33.0	0.0								
benzenic compounds													
C ₆ H ₆	benzene	82.6	0.7	84.2	1.6	49.0	0.5	48.7	0.3	5525.4	0.7	5523.9	1.6

TABLE 11. Experimental and estimated values for hydrocarbons (data in kJ·mol⁻¹)—Continued













Compound		Experimental gas-phase enthalpy of formation ^a		Estimated value and difference between exp. and fitted gas-phase enthalpy of formation		Experimental condensed-phase enthalpy of formation ^a		Estimated value and difference between exp. and fitted condensed phase enthalpy of formation		Atomization enthalpy ^b		Estimated value and difference between exp. and fitted atomization enthalpy	
		Value	Error	Value	Diff.	Value	Error	Value	Diff.	Value	Error	Value	Diff.
C ₇ H ₈	benzene, methyl	50.5	0.5	50.3	0.2	12.4	0.5	11.1	1.3	6710.2	0.5	6710.4	0.2
C ₈ H ₆	phenylacetylene	306.6 ^c	1.7	306.6	0.0	283.5	4.2	283.5	0.0	6734.8	1.7	6734.8	0.0
C ₈ H ₈	phenylethylene	148.0	1.4	148.0	0.0	103.8	1.1	103.8	0.0	7329.4	1.4	7329.4	0.0
C ₈ H ₁₀	benzene, ethyl	30.0	1.0	29.8	0.2	-12.3	0.8	-12.3	0.0	7883.4	1.0	7883.5	0.2
	benzene, 1,2-dimethyl	19.1	1.0	19.9	0.8	-24.4	1.0	-23.4	1.0	7894.3	1.0	7893.5	0.8
	benzene, 1,3-dimethyl	17.3	0.7	16.4	0.9	-25.4	0.7	-26.5	1.1	7896.1	0.7	7896.9	0.9
	benzene, 1,4-dimethyl	18.1	1.0	16.4	1.7	-24.4	1.0	-26.5	2.1	7895.3	1.0	7896.9	1.7
C ₉ H ₁₀	2-phenylpropene	118.3 ^c	1.4	118.3	0.0	70.5	1.1	70.5	0.0	8511.7	1.4	8511.7	0.0
C ₉ H ₁₂	benzene, propyl	7.9	0.7	9.1	1.2	-38.3	0.7	-37.7	0.6	9058.1	0.7	9056.9	1.3
	benzene, i-propyl	4.0	1.0	2.2	1.8	-41.1	1.0	-40.8	0.3	9062.0	1.0	9063.8	1.8
	benzene, 1-ethyl,2-methyl	1.3	1.0	-0.6	1.9	-46.4	1.0	-46.8	0.4	9064.7	1.0	9066.6	1.9
	benzene, 1-ethyl,3-methyl	-1.8	1.1	-4.0	2.2	-48.7	1.1	-49.8	1.1	9067.8	1.1	9070.1	2.2
	benzene, 1-ethyl,4-methyl	-3.2	1.3	-4.0	0.8	-49.8	1.3	-49.8	0.0	9069.2	1.3	9070.1	0.8
	benzene, 1,2,3-trimethyl	-9.5	1.2	-11.3	1.8	-58.5	1.2	-57.8	0.7	9075.5	1.2	9077.3	1.8
	benzene, 1,2,4-trimethyl	-13.9	1.0	-14.0	0.1	-61.8	1.0	-61.0	0.8	9079.9	1.0	9080.0	0.1
	benzene, 1,3,5-trimethyl	-15.9	1.3	-17.4	1.5	-63.4	1.3	-64.0	0.6	9081.9	1.3	9083.4	1.5
C ₁₀ H ₁₄	benzene, butyl	-11.8	1.2	-11.6	0.2	-63.2	1.0	-63.1	0.1	10230.5	1.2	10230.2	0.3
	benzene, (1-methylpropyl)	-18.4	1.5	-16.6	1.8	-66.4	1.2	-64.5	1.9	10237.1	1.5	10235.3	1.8
	benzene, (2-methylpropyl)	-21.9	1.6	-18.3	3.6	-69.8	1.3	-68.2	1.6	10240.6	1.6	10236.9	3.7
	benzene, t-butyl	-23.0	1.5	-23.0	0.0	-70.7	1.2	-70.7	0.0	10241.7	1.5	10241.7	0.0
	benzene, 1-methyl, 2-propyl			-21.3		-72.5	0.9	-72.2	0.3			10240.0	
	benzene, 1-methyl, 3-propyl			-24.7		-76.2	1.1	-75.2	1.0			10243.4	
	benzene, 1-methyl, 4-propyl			-24.7		-75.1	0.9	-75.2	0.1			10243.4	
	benzene, 1,2-diethyl			-21.0		-68.5	0.9	-70.2	1.7			10239.8	
	benzene, 1,3-diethyl			-24.5		-73.5	1.0	-73.2	0.3			10243.2	
	benzene, 1,4-diethyl			-24.5		-72.8	0.9	-73.2	0.4			10243.2	
	benzene, 1-i-propyl, 2-methyl			-28.2		-73.3	0.9	-75.3	2.0			10246.9	
	benzene, 1-i-propyl, 3-methyl			-31.7		-78.6	1.0	-78.4	0.2			10250.4	
	benzene, 1-i-propyl, 4-methyl			-31.7		-78.0	1.0	-78.4	0.4			10250.4	
	benzene, 1-ethyl, 2,3-dimethyl			-31.8		-80.5	1.2	-81.2	0.7			10250.5	
	benzene, 2-ethyl, 1,3-dimethyl			-31.8		-80.1	1.2	-81.2	1.1			10250.5	
	benzene, 4-ethyl, 1,2-dimethyl			-34.4		-86.0	1.0	-84.3	1.7			10253.2	
	benzene, 1-ethyl, 2,4-dimethyl			-34.4		-84.1	1.2	-84.3	0.2			10253.2	
	benzene, 2-ethyl, 1,4-dimethyl			-34.4		-84.8	1.1	-84.3	0.5			10253.2	
	benzene, 1-ethyl, 3,5-dimethyl			-37.9		-87.8	1.1	-87.4	0.4			10256.6	
	benzene, 1,2,3,4-tetramethyl			-38.4		-90.2	1.2	-90.2	0.0			10257.0	
	benzene, 1,2,3,5-tetramethyl			-45.2		-96.4	1.1	-95.4	1.0			10263.9	
	benzene, 1,2,4,5-tetramethyl	-47.1	1.9	-44.4	2.7			-95.5		10265.8	1.9	10263.1	2.7
C ₁₁ H ₁₆	benzene, pentyl					-89.4	4.2	-88.5	0.9				
	benzene, pentamethyl	-67.2	2.2	-65.4	1.8			-122.6		11438.6	2.2	11436.7	1.8
C ₁₂ H ₁₈	benzene, hexamethyl	-77.4	2.5	-78.0	0.6			-145.8		12601.4	2.5	12602.0	0.6
biphenyl compounds													
C ₁₂ H ₁₀	biphenyl	182.0 ^c	0.7	179.1	2.9					10598.0	0.7	10600.9	2.9
C ₁₃ H ₁₂	biphenyl, 2-methyl	152.8 ^c	1.5	148.7	4.1					11779.9	1.5	11784.0	4.1
	biphenyl, 4-methyl	138.2 ^c	2.9	145.2	7.0					11794.5	2.9	11787.5	7.0
polyaromatic hydrocarbons													
C ₁₀ H ₈	Naphtalene	150.3	1.4	150.7	0.4					8760.4	1.4	8760.0	0.4
C ₁₁ H ₁₀	Naphtalene, 1-methyl	116.9 ^c	2.7	127.1	10.2					9946.5	2.7	9936.2	10.2
	Naphtalene, 2-methyl	106.7	1.7	116.8	10.1					9956.7	1.7	9946.5	10.2
C ₁₂ H ₁₂	Naphtalene, 1,8-dimethyl	108.7	1.5	103.6	5.1					11107.3	1.5	11112.5	5.1
													
	Naphtalene, 2,3-dimethyl	76.1	1.0	86.4	10.3					11139.9	1.0	11129.6	10.3
C ₁₄ H ₁₀	Anthracene	230.9	2.2	217.3	13.6					11982.5	2.2	11996.1	13.6
													
	Phenanthrene	207.5	1.7	241.0	33.5					12005.9	1.7	11972.4	33.5
													

TABLE 11. Experimental and estimated values for hydrocarbons (data in $\text{kJ}\cdot\text{mol}^{-1}$)—Continued

Compound		Experimental gas-phase enthalpy of formation ^a		Estimated value and difference between exp. and fitted gas-phase enthalpy of formation		Experimental condensed-phase enthalpy of formation ^a		Estimated value and difference between exp. and fitted condensed phase enthalpy of formation		Atomization enthalpy ^b		Estimated value and difference between exp. and fitted atomization enthalpy	
		Value	Error	Value	Diff.	Value	Error	Value	Diff.	Value	Error	Value	Diff.
C ₁₆ H ₁₀	Benzo[d,e,f]phenanthrene (pyrene) 	225.7	1.2	225.7	0.0					13421.0	1.2	13421.0	0.0
C ₁₈ H ₁₂	Benz[a]anthracene 	293.0	4.2	279.5	13.5					15223.0	4.2	15236.5	13.5
	Benz[b]anthracene 	291.4	9.3	283.8	7.6					15224.6	9.3	15232.2	7.6
	Benz[a]phenantrene (chrysene) 	269.8	6.6	275.3	5.5					15246.2	6.6	15240.8	5.5
	9,10-Benzo phenantrene 	274.2	4.3	271.0	3.2					15241.8	4.3	15245.1	3.2
	Benz[c]phenantrene 	291.2	4.6	303.3	12.1					15224.8	4.6	15212.8	12.1
C ₂₀ H ₁₀	Corannulene 	460.6 ^c	6.5	451.5	9.1					16052.8	6.5	16061.9	9.2
C ₂₀ H ₁₂	Perylene 	319.4 ^c	2.2	319.4	0.0					16630.0	2.2	16630.0	0.0
C ₂₄ H ₁₂	Coronene 	307.5 ^c	9.8	307.5	0.0					19508.4	9.8	19508.6	0.0

^aValues taken from Pedley,⁷ unless stated otherwise, ^bChase *et al.*¹¹ and note 12, ^cNIST Webbook,^{13d} note 14, ^eSimões and Beauchamp¹⁰

Beauchamp.¹⁰ As stated by the authors those values are consistent with the enthalpies of formation tabulated by Pedley and Rylance, *Sussex-N.P.L. Computer Analyzed Thermochemical Data: Organic and Organometallic Compounds* (University of Sussex: Brighton, 1977), a previous version of Pedley compilation data.⁷

5. Results

5.1. Parameters

The application of the procedure described above to the set of data in Table 11 (200 gas-phase enthalpies of formation, 164 condensed-phase enthalpies of formation, and 200 atomization enthalpies) led to three sets of 103 Laidler terms. Two of these sets are for gas- and condensed-phase enthalpies of formation, and the other for the atomization enthalpies. The obtained values are presented in Table 12.

Due to the lack of experimental data needed to define some of the parameters, these cases are marked in the table as not available (n.a.). Columns five and six of Table 12

display how many times each term was used to describe the energetics of the set of compounds in Table 11. A low number means that a parameter was required just a few times and therefore is more prone to changing when data for new compounds become available; a large number means that a parameter had been widely used and its value should be very robust. To estimate the desired property for a given compound, a sum of all the suitable terms and steric factors in the molecule must be made. The parameters in Table 12 are given with two decimals, to avoid roundoff errors. To minimize these errors when estimating a value, an Excel datasheet is supplied as supplementary material.²⁴ If care is not taken the errors can be quite large, particularly in large molecules.

Figures 11 and 12 show the estimated versus the experimental enthalpies of formation for the gas and condensed phase, respectively. The average difference between the estimated and the experimental values is $1.87\text{ kJ}\cdot\text{mol}^{-1}$ for the 200 gas-phase compounds and $1.38\text{ kJ}\cdot\text{mol}^{-1}$ for the 164 compounds in the condensed phase. However if the polyaro-

TABLE 12. Obtained parameters and number of times they were used (frequency)

Parameter	Parameter value			Number of times parameter was used	
	Gas phase ^a	Condensed phase ^a	Atomization ^a	Gas phase and atomization	Condensed phase
C3H	17.60	− 12.53	402.09	43	44
C2H	− 6.54	− 12.91	411.06	112	105
C1H	− 13.06	− 16.81	412.53	86	82
C0H	− 18.60	n.a.	415.77	1	0
C1C1	− 4.45	7.28	348.94	1	1
C1C2	− 6.65	2.26	350.77	80	80
C1C3	− 11.38	3.14	355.31	39	40
C1C4	− 2.77	3.00	354.20	24	22
C2C2	− 7.64	0.42	351.22	65	58
C2C3	− 10.41	3.05	353.86	29	29
C2C4	0.92	5.01	350.02	10	10
C3C3	− 8.91	9.13	352.16	6	6
C3C4	7.49	15.54	343.26	3	3
C4C4	25.73	15.63	332.55	1	1
D1D1	− 0.28	n.a.	523.40	1	0
D1D2	1.59	3.51	519.15	22	15
D1D3	6.44	4.14	511.12	14	12
D2D2	3.93	6.01	515.05	33	25
D2D3	12.15	9.99	502.37	9	9
D3D3	25.50	16.89	485.52	1	1
C1D2	11.84	5.04	379.16	26	20
C1D3	13.92	19.14	388.87	21	20
C2D2	11.63	4.00	379.35	32	27
C2D3	14.87	19.43	387.07	11	11
C3D2	7.92	5.96	382.95	7	7
C3D3	14.41	22.82	387.54	2	2
C4D2	21.38	9.58	376.73	5	5
C4D3	32.81	32.33	376.48	2	1
D1H	13.20	9.72	432.36	42	28
D2H	19.20	25.23	437.09	62	50
Z11	3.74	3.46	− 3.64	19	16
Z14	16.91	16.36	− 16.84	1	1
Z44	39.65	45.40	− 39.80	1	1
T1T1	22.04	25.34	698.55	1	1
T1T2	58.54	61.08	695.54	13	9
T2T2	96.58	94.27	690.89	13	5
C1T2	64.62	63.14	430.59	8	3
C2T2	62.79	61.39	431.98	17	6
C3T2	49.59	65.24	444.56	1	1
C4T2	71.99	67.46	430.04	1	1
T1H	102.33	91.68	472.04	14	10
D1Dd	68.78	− 0.22	551.07	6	2
D2Dd	74.62	139.94	543.30	4	1
D3Dd	84.44	144.57	529.57	1	1
DdDd	20.92	n.a.	620.35	1	0
Cd2d2	14.46	− 7.87	423.91	9	2
Cd2d3	20.77	7.73	428.59	2	1
Cd3d3	30.18	29.82	430.11	2	1
Cd2t2	82.84	61.80	459.11	2	2
Cd3t2	90.57	85.96	462.47	1	1
Ct2t2	133.38	121.25	512.47	1	1
ZS3	111.56	107.10	− 111.42	2	2
ZS4	110.58	105.31	− 110.34	1	1
ZS5	25.01	19.88	− 24.76	2	2
ZS6	− 2.28	− 6.75	2.56	3	3
ZS7	26.93	21.22	− 26.53	1	1
ZS8	41.35	35.52	− 40.89	1	1
ZS9	53.67	47.42	− 53.15	1	1
ZS10	52.89	47.32	− 52.31	1	1
ZD4	124.93	n.a.	− 125.43	1	0

TABLE 12. Obtained parameters and number of times they were used (frequency).—Continued

Parameter	Parameter value			Number of times parameter was used	
	Gas phase ^a	Condensed phase ^a	Atomization ^a	Gas phase and atomization	Condensed phase
ZD5	22.26	16.12	−22.58	4	4
ZD6	5.37	3.34	0.65	2	2
ZD7	21.19	n.a.	−21.55	1	0
ZD8	24.10	14.35	−24.43	1	1
C0R	202.70	n.a.	−23.53	1	0
C1R	187.80	n.a.	−6.36	6	0
C2R	181.57	n.a.	4.89	2	0
C3R	195.69	n.a.	5.96	1	0
A2A2	6.04	3.21	485.02	36	36
A2A3	14.02	13.27	478.88	26	38
A3A3	16.93	17.09	460.25	8	14
C1A3	−2.65	−2.34	396.84	16	24
C2A3	−3.37	−2.15	397.10	7	20
C3A3	−6.42	2.41	399.97	2	5
C4A3	10.73	7.73	390.36	1	1
A2H	7.99	4.90	435.62	39	39
ZA11	8.51	9.29	9.04	5	9
ZA14	n.a.	n.a.	n.a.	0	0
ZA44	n.a.	n.a.	n.a.	0	0
ZA1'1	8.13	9.35	9.43	2	5
ZA1'4	n.a.	n.a.	n.a.	0	0
ZA1'1'	11.91	11.40	5.64	2	1
ZA1'4'	n.a.	n.a.	n.a.	0	0
ZA4'1	n.a.	n.a.	n.a.	0	0
ZA4'4'	n.a.	n.a.	n.a.	0	0
D2A3	8.69	−8.27	432.47	1	1
D3A3	18.61	14.33	433.49	1	1
T2A3	53.59	66.86	491.24	1	1
Ca3a3	−5.17	n.a.	449.05	3	0
M0	17.05	n.a.	460.12	10	0
M2	15.93	n.a.	458.99	3	0
M4	2.45	n.a.	475.34	2	0
M0M0	34.47	n.a.	443.63	6	0
M0M2	n.a.	n.a.	n.a.	0	0
M2M2	18.09	n.a.	462.60	1	0
A2M0	8.38	n.a.	476.19	9	0
A2M0'	−5.62	n.a.	490.20	4	0
A2M2	5.43	n.a.	480.42	3	0
A2M2'	5.45	n.a.	480.39	1	0
A3M0	26.66	n.a.	459.75	1	0
A3M0'	n.a.	n.a.	n.a.	0	0
A3M2	n.a.	n.a.	n.a.	0	0
A3M2'	n.a.	n.a.	n.a.	0	0

^an.a.—not available.

matic compounds are not taken into account the average difference for the gas phase values (187 compounds) drops to $1.28 \text{ kJ} \cdot \text{mol}^{-1}$. The linear equations that best fit the data are (estimated value = $0.9997 \times \text{experimental value} + 0.0044$, with a correlation coefficient of 0.9999) and (estimated value = $0.9984 \times \text{experimental value} - 0.1760$, with a correlation coefficient of 0.9999) for gas phase and liquid phase, respectively. In these conditions (excluding the polyaromatic compounds), the maximum deviations are 8.1 and $8.0 \text{ kJ} \cdot \text{mol}^{-1}$ for gas phase and liquid phase. It should be noted that the maximum deviations presented are obtained for the same compound (2,2,4-trimethyl-pentane) which poses some

doubts on the correctness of the experimental values published in this case.

5.2. Values Predicted Using the Obtained Parameters

A good test to the method and to the obtained parameters is predicting enthalpies of formation of compounds not used in the fitting, but for which experimental data exist. A set of compounds, none of which were used for the parameterization, is presented in Table 13 and their experimental enthalpies of formation are compared with data estimated from

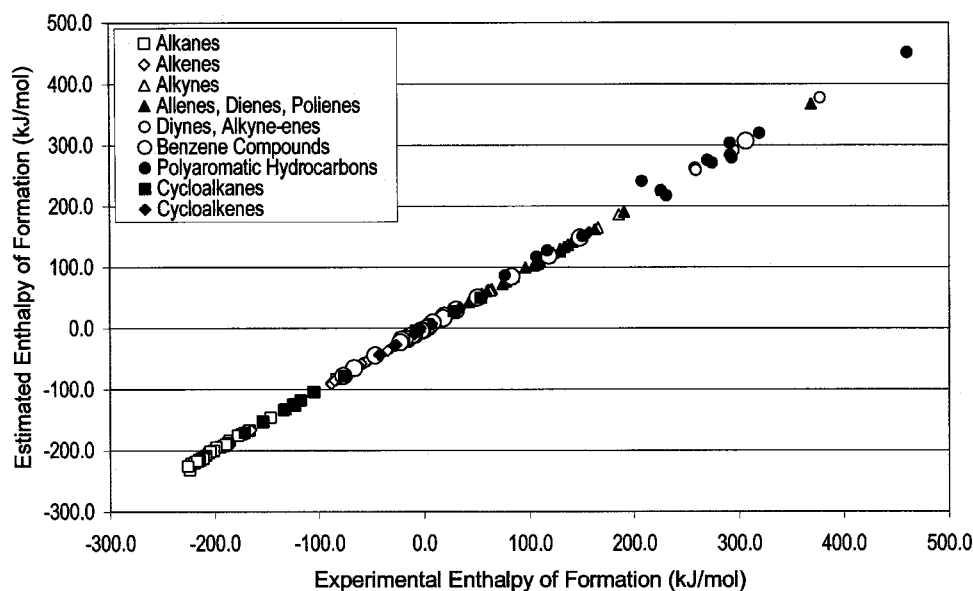


FIG. 11. Estimated vs experimental gas-phase enthalpies of formation.

several methods.^{5,15,16} This set includes linear and branched alkanes (nonane, decane, dodecane, hexadecane, and dotriacontane; 2,2,5-trimethylhexane, 2,3,5-trimethylhexane and 5,5,7,7-tetramethylundecane), linear and branched alkenes (octane, 1-decene, 1-hexadecene; Z-2,2-dimethyl-3-hexene, and E-2,2-dimethyl-3-hexene), linear alkynes (1-decyne, 2-decyne, and 3-decyne), and polyalkenes (1,2,6,7-octatetraene). In every case, the difference between the experimental and estimated values (using the Laidler terms determined above) is very close to the errors assigned to the experimental values. The excellent ability of this new parameterization to distinguish between isomers (even between 2 and 3 decynes) should also be stressed. A comparison of the deviations obtained with the “best” additive methods available in the literature shows that the errors associated with the estimation are comparable in all of them.

Also the estimated values for the enthalpy of formation for some cyclic and polyaromatic hydrocarbons are presented in Table 14 and compared with experimental values from the literature.^{7,13,17,18} The absolute deviation for these compounds is higher (on average) than for other hydrocarbons but comparable to the deviation found for the polyaromatic hydrocarbons used to determine the parameters (see Table 11). Maybe some of the experimental values for those compounds had to be reevaluated.

An attempt was made to estimate the value of the enthalpy of formation, in the gas phase, of C_{60} . There should be special attention paid the literature values, since not all of them are in agreement; $\Delta_f H^\circ(C_{60}, g) = 2511.3 \pm 13.7 \text{ kJ} \cdot \text{mol}^{-1}$,¹⁹ $2651.3 \pm 17.1 \text{ kJ} \cdot \text{mol}^{-1}$,²⁰ $2507.1 \pm 17.4 \text{ kJ} \cdot \text{mol}^{-1}$,²¹ and $2506.8 \pm 12.4 \text{ kJ} \cdot \text{mol}^{-1}$.²² The estimated value, using the Laidler terms calculated in the present paper, is 2847 kJ

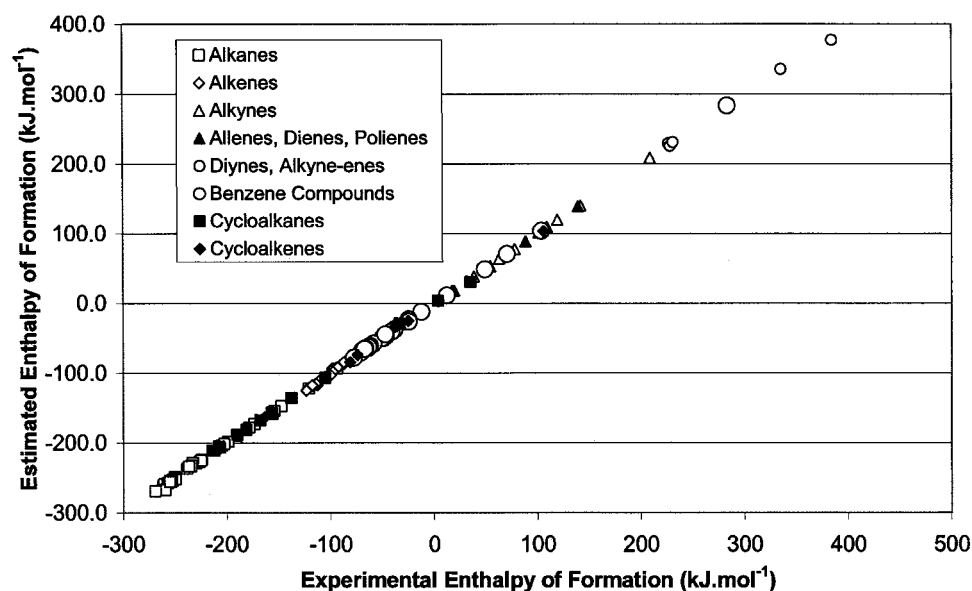


FIG. 12. Estimated vs experimental condensed-phase enthalpies of formation.


TABLE 13. Comparison between experimental and predicted gas-phase enthalpies of formation (data in $\text{kJ}\cdot\text{mol}^{-1}$)

Compound			Estimated in this paper		Estimated in literature					
					NIST ^b		Domalski ^c		Cohen ^d	
Formula	Name	Experiment ^a	Value	Dif. ^e	Value	Dif. ^e	Value	Dif. ^e	Value	Dif. ^e
C ₈ H ₁₀	1,2,6,7-octatetraene	369.0	367.4	1.6	371	2.0	369.4	0.4	–	
C ₈ H ₁₆	octene	−81.3±1.2	−83.0	1.7	−82.8	1.5	−83.0	1.7	−83.3	2.0
C ₈ H ₁₆	(Z)-3-hexene, 2,2-dimethyl	−89.3±2.8	−92.5	3.2	−94.6	5.3	−91.6	1.1	−90.0	0.7
C ₈ H ₁₆	(E)-3-hexene, 2,2-dimethyl	−107.7±1.6	−109.5	1.8	−111	3.3	−108.8	1.1	−108.4	0.7
C ₉ H ₂₀	nonane	−228.2	−229.1	0.9	−229	0.8	−228.9	0.9	−230.1	1.9
C ₉ H ₂₀	hexane, 2,2,5-trimethyl	−253.1	−252.7	0.4	−250	3.1	−256.3	3.2	−251.5	1.6
C ₉ H ₂₀	hexane, 2,3,5-trimethyl	−242.6	−242.8	0.2	−244	1.4	−246.2	3.6	−243.5	0.9
C ₁₀ H ₁₈	1-decyne	41.9±3.4 ^f	40.4	1.5	41.8	0.1	42.9	1.0	41.0	0.9
C ₁₀ H ₁₈	2-decyne	23.6±3.4 ^f	22.3	1.3	23	0.6	22.8	0.8	20.5	3.1
C ₁₀ H ₁₈	3-decyne	21.8±3.3 ^f	21.4	0.4	23	1.2	23.8	2.0	21.8	0.0
C ₁₀ H ₂₀	1-decene	−123.3±1.8	−124.4	1.1	−124	0.7	−124.3	1.0	−125.1	1.8
C ₁₀ H ₂₂	decane	−249.5	−249.8	0.3	−250	0.5	−249.6	0.1	−251.0	1.5
C ₁₂ H ₂₆	dodecane	−289.4±2.1	−291.2	1.8	−291	1.6	−290.8	1.4	−292.9	3.5
C ₁₃ H ₃₂	undecane, 5,5,7,7-tetramethyl	−366.6	−377.9	11.3	−363	3.6	−377.8	11.2	−371.5	4.9
C ₁₆ H ₃₂	1-hexadecene	−248.4±2.4	−248.7	0.3	−247	1.4	−248.1	0.3	−250.6	2.2
C ₁₆ H ₃₄	hexadecane	−374.8	−374.1	0.7	−374	0.8	−373.3	1.5	−376.6	1.8
C ₃₂ H ₆₆	dotriacontane	−697.2±9.6	−705.6	8.4	−702.9	5.7	−703.4	6.2	−711.3	14.1
Average deviation				2.2		2.0		2.2		2.6

^aValues taken from Pedley,⁷ unless stated otherwise, ^bStein and Brown,⁵ ^cDomalski *et al.*,¹⁵ ^dCohen,¹⁶ ^eabsolute deviation, ^fNIST Webbook.¹³

$\cdot\text{mol}^{-1}$. Independently of each one of the experimental values is the best one, the estimated value is away by some 200–350 $\text{kJ}\cdot\text{mol}^{-1}$. This can be due to additional stabilization in the very large aromatic system of C₆₀, but can also support the fact that probably some of the experimental values for the polyaromatic hydrocarbons used to determine the parameters had to be reevaluated (e.g., phenanthrene with a deviation of 33.5 $\text{kJ}\cdot\text{mol}^{-1}$).

TABLE 14. Comparison between experimental and predicted gas-phase enthalpies of formation for cyclic and polyaromatic hydrocarbons (data in $\text{kJ}\cdot\text{mol}^{-1}$)

Compound			Estimated in this paper	
Formula	Name	Experimental	Value	Dif. ^e
C ₆ H ₈	1,3-cyclohexadiene	104.6±0.6 ^a	94.0	10.6
C ₈ H ₁₆	cyclohexane,1,1-dimethyl	−180.8±2.0 ^b	−180.3	0.5
C ₁₀ H ₁₂	 tetralin	26.0±2.0 ^a	26.9	0.7
C ₁₂ H ₈	acenaphthylene	263.8±3.4 ^c	269.2	5.4
C ₁₂ H ₁₀	acenaphthene	155.9±2.5 ^c	168.9	13.0
C ₁₃ H ₁₀	fluorene	169.3±4.1 ^d	187.3	18.0
C ₁₄ H ₈	pyracylene	410.3±5.6 ^c	387.7	22.6
C ₁₄ H ₁₂	pyracene	174.3±5.3 ^c	187.2	12.9

^aNIST Webbook,¹³ ^bPedley,⁷ ^cDiogo *et al.*,¹⁷ ^dSabbah and Antipine,¹⁸ ^eabsolute deviation.

5.3. Physical Meaning of the Parameters

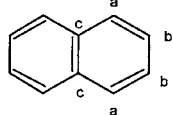
As stated above, the Laidler terms for atomization enthalpy should reflect the strength of the chemical bonds. If this is true, those parameters can be correlated with physical properties of the compounds (e.g., bond lengths) and can be used, together with bond dissociation enthalpies, to predict reorganization enthalpies of the fragments.

In Table 15 some experimental bond lengths for hydrocarbons²³ are presented, together with the calculated parameters that correspond to each type of bond. When one of the parameters appears in more than one compound, the average of the experimental distances was taken to correlate with the parameter values (Figs. 13 and 14). The carbon–carbon bond lengths correlate quite well with the parameters obtained for the atomization enthalpy (Fig. 13). The trend line presented on the graph is a power function ($y = -60.05 + 1184.43 \times x^{-2.36}$, $r = 0.991$). Also for the C–H bonds there is a correlation (if the C–H bond in methane is excluded) between the C–H bond lengths and the Laidler terms ($y = 297.82 + 372.19 \times x^{-10.88}$, $r = 0.834$) (Fig. 14). The existence of these correlations strongly support the fact that the parameters calculated for the atomization enthalpy are a good approximation to the intrinsic strength of a bond.

Considering that the obtained parameters for the atomization enthalpies represent the intrinsic bond strength (can be identified with bond enthalpy terms, E) they can be used to predict reorganization enthalpies associated with almost any

TABLE 15. Experimental bond lengths for a variety of compounds in gas phase.

Compound		Bond	Experimental distance ²⁰ (Å)	Correspondent parameter
Formula	Name			
CH ₄	methane	C–H	1.087	C0H
C ₂ H ₆	ethane	C–C	1.535	C1C1
		C–H	1.094	C1H
C ₃ H ₈	propane	C–C	1.532	C1C2
		C–H	1.107	C1H
C ₄ H ₁₀	butane	C–C	1.531	C1C2
		C–H	1.117	C1H
(C ^b H ₃) ₃ C ^a H	<i>i</i> -butane	C–C	1.535	C1C3
		C ^a –H	1.122	C3H
		C ^b –H	1.113	C1H
C(CH ₃) ₄	neo-pentane	C–C	1.537	C1C4
		C–H	1.114	C1H
HC ^a [C ^b (C ^c H ₃) ₃] ₃	tri- <i>t</i> -butyl methane	C ^a –C ^b	1.611	C3C4
		C ^b –C ^c	1.548	C1C4
		C ^c –H	1.111	C1H
C ₂ H ₄	ethene	C=C	1.339	D1D1
		C–H	1.087	D1H
C ^c H ₃ C ^b H=C ^a H ₂	propene	C ^a =C ^b	1.341	D1D2
		C ^b –C ^c	1.506	C1D2
		C ^a –H	1.104	D1H
		C ^c –H	1.117	C1H
C ₄ H ₈	2-butene (cis)	C=C	1.346	D2D2
		C–C	1.506	C1D2
C ₄ H ₈	2-butene (trans)	C=C	1.347	D2D2
		C–C	1.508	C1D2
(C ^b H ₃) ₂ C=C ^a H ₂	2-methyl propene	C=C	1.342	D1D3
		C–C	1.508	C1D3
		C ^a –H	1.10	D1H
		C ^b –H	1.119	C1H
HC≡CH	ethyne	C≡C	1.203	T1T1
		C–H	1.060	T1H
HC ^a ≡CC ^b H ₃	propyne	C≡C	1.206	T1T2
		C–C	1.459	C1T2
		C ^a –H	1.056	T1H
		C ^b –H	1.105	C1H
H ₃ CC≡CCH ₃	2-butyne	C≡C	1.214	T2T2
		C–C	1.468	C1T2
		C–H	1.116	C1H
H ₂ C=C=CH ₂	allene	C=C	1.308	D2Dd
		C–H	1.087	D1H
H ₂ C ^a =C ^b H–	1,3-butadiene	C ^b –C ^b	1.467	Cd2d2
C ^b H=C ^a H ₂		C ^a =C ^b	1.349	D1D2
HC ^a ≡C ^b –	1,3-butadiyne	C ^b –C ^b	1.384	C1t2
C ^b ≡C ^a H		C ^a =C ^b	1.218	T1T2
		C–H	1.090	T1H
H ₂ C ^a =C ^b =C ^b =C ^a H ₂	butatriene	C ^b =C ^b	1.280	DdDd
		C ^a =C ^b	1.320	D2Dd
		C–H	1.080	D1H
H ₂ C ^a =C ^b H–	vinylacetylene	C ^a =C ^b	1.344	D1D2
C ^c =C ^d H		C ^b –C ^c	1.434	Cd2t2
		C ^c ≡C ^d	1.215	T1T2
		C ^a –H	1.110	D1H
		C ^d –H	1.090	T1H
C ₆ H ₆	benzene	C=C	1.399	A2A2
		C–H	1.101	A2H
C ^a ₅ H ₅ C ^b C ^c H ₃	toluene	C ^a =C ^b	1.399	A2A3
		C ^b –C ^c	1.524	C1A3
	naphthalene	C ^a –C ^b	1.37	A2A2
		C ^b –C ^b	1.41	A2A2
		C ^a –C ^c	1.42	A2M0
		C ^c –C ^c	1.42	M0



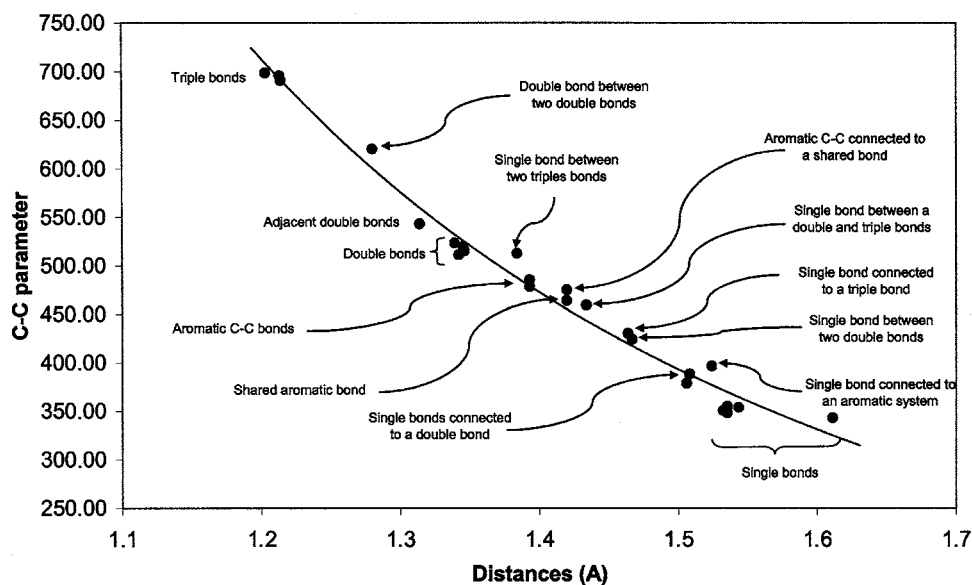


FIG. 13. Carbon-carbon Laidler terms vs experimental bond lengths.

fragment, according to Scheme 3 (where X can be C or H).

It should be stressed that the reorganization enthalpies of atoms are taken as zero, meaning that the bond enthalpy terms are not really **intrinsic bond enthalpies**. If they are, all the reorganization enthalpies should be negative (otherwise the fragment would not reorganize) (for a detailed discussion see Simões and Beauchamp¹⁰ and references therein). However this is a useful definition and is used in almost all the literature. In Table 16 some examples are presented being the reorganization enthalpy values calculated using the previous assumption compared with the literature values, when possible (Table 17).

5.4. Using the Same Procedure for Other Properties

The same procedure used in this paper to estimate enthalpies of formation or atomization enthalpies can be extended

to other quantities, assuming that the property under study can be thought of as additive. This is the case, for example, for the heat capacity, C_p , both in gas phase and in condensed phase. As a sample, Table 18 presents the C_p values for alkanes, alkenes, and alkynes in the gas phase and for the two former families also in the liquid phase, and Table 19 provides the corresponding parameter values, taken from the fitting procedure. The C_p values estimated using those parameters (even for the compounds that have no experimental values) are also included in Table 18 and compared with the experimental ones when possible. The average deviation from experimental values is

$$1.06 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \text{ for the gas phase (60 compounds)}$$

and

$$0.86 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \text{ for the liquid phase (36 compounds),}$$

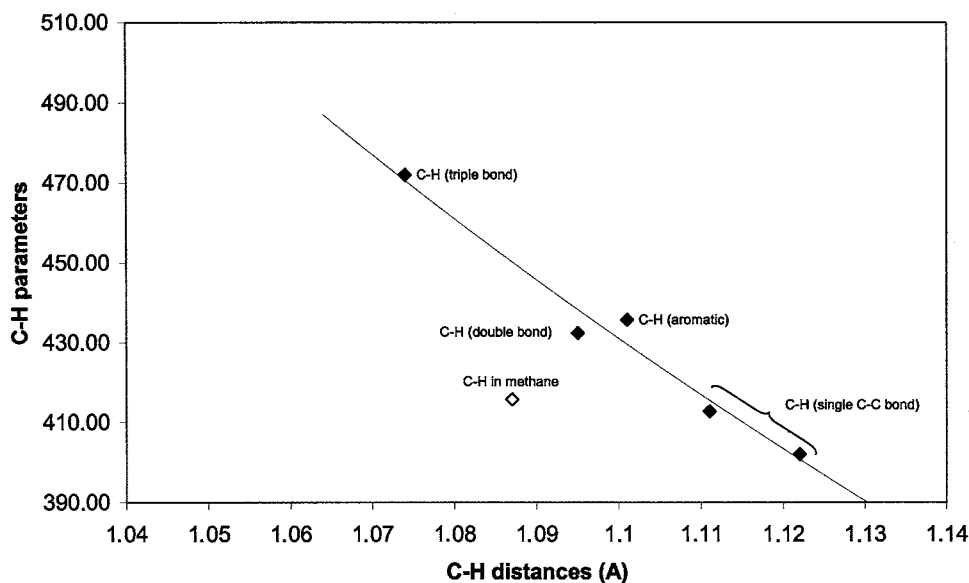
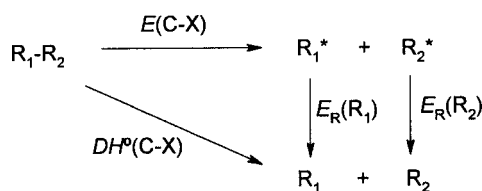


FIG. 14. C-H Laidler terms vs experimental bond lengths.



Scheme 3.

with the highest deviations being 5.5 and 3.4 J·K⁻¹·mol⁻¹, respectively.

6. Conclusion

Based on a model proposed by Laidler,² a series of parameters (bond terms) are proposed which permit the estimation of the enthalpy of formation at 298.15 K of hydrocarbon compounds in the gas and liquid phases as well as the atomization enthalpy. The proposed values provide a good estimation of these properties for very different families of compounds ranging from alkanes to polyaromatic hydrocarbons. The accuracy obtained is comparable to other additivity methods from the literature^{5,15,16} with the advantage that, to the parameters for the atomization enthalpy, a physical meaning can be associated with them. This fact allows the calculation of reorganization enthalpies for a great variety of fragments.

The data base used seems to be essentially error free, but some compounds (very few) show a deviation that is higher than all the others in their family of compounds and their experimental values should be reevaluated. As an example, Fig. 15 shows the deviations between experimental and esti-

TABLE 17. Comparison of reorganization enthalpies

Fragment	Reorganization energy ^a kJ·mol ⁻¹	Reorganization energy ^b kJ·mol ⁻¹
CH ₃	23.5, 14.3	24
C ₂ H ₅	8.3, 6.2	10
C ₃ H ₇	6.2, 3.8	7
<i>i</i> -C ₃ H ₇	-4.4, -3.0	-1
C ₄ H ₉	5.2, 2.6	7
<i>t</i> -C ₄ H ₉	-5.8, -9.3	-8
C ₂ H ₃	28.1, 28.0	38
CH ₂	98.0	
CH	131.4	
C ₆ H ₅	29.8	44
C ₆ H ₅ CH ₂	-45.0	-43

^aTaken from Table 15.

^bSimões and Beauchamp.¹⁰

mated gas phase values for the enthalpy of formation for all alkanes from C₁ to C₈. All values are equal to or less than 2.5 kJ·mol⁻¹, with two exceptions: 2,3-dimethylpentane (4.0 kJ·mol⁻¹) and 2,2,4-trimethylpentane (8.1 kJ·mol⁻¹). While the deviation for the first compound can be assumed to be due to a limitation of the fitting method, the second one seems clearly be due to an experimental value that needs to be reevaluated. A remeasurement of the enthalpy of combustion (or reaction) or a reassessment of the enthalpy of formation for this particular compound is encouraged.

The enlargement of the same methodology to compounds containing atoms other than carbon and hydrogen is under study. The next step will be the compounds with carbon, hydrogen, and oxygen.

TABLE 16. Reorganization enthalpies of a variety of fragments

Fragments		Bond Dissociation Enthalpy (D) (kJ·mol ⁻¹) ^a	Bond enthalpy term		Reorganization energy (kJ·mol ⁻¹) ^b	
R ₁	R ₂		Parameter	E(kJ·mol ⁻¹)	R ₁	R ₂
CH ₃	H	439.3	C0H	415.77	23.5	0
CH ₃	CH ₃	377.6	C1C1	348.94	14.3	14.3
C ₂ H ₅	H	420.8	C1H	412.53	8.3	0
C ₂ H ₅	C ₂ H ₅	363.7	C2C2	351.22	6.2	6.2
C ₃ H ₇	H	418.7	C1H	412.53	6.2	0
C ₃ H ₇	C ₃ H ₇	358.9	C2C2	351.22	3.8	3.8
<i>i</i> -C ₃ H ₇	H	406.7	C2H	411.06	-4.4	0
<i>i</i> -C ₃ H ₇	<i>i</i> -C ₃ H ₇	346.1	C3C3	352.16	-3.0	-3.0
C ₄ H ₉	H	417.7	C1H	412.53	5.2	0
C ₄ H ₉	C ₄ H ₉	356.5	C2C2	351.22	2.6	2.6
<i>t</i> -C ₄ H ₉	H	396.2	C3H	401.97	-5.8	0
<i>t</i> -C ₄ H ₉	<i>t</i> -C ₄ H ₉	314.0	C4C4	332.55	-9.3	-9.3
C ₂ H ₃	H	460.5	D1H	432.36	28.1	0
C ₂ H ₃	C ₂ H ₃	480.0	Cd2d2	423.91	28.0	28.0
CH ₂	CH ₂	719.5	D1D1	523.40	98.0	98.0
C ₂ H	H	556.3	T1H	472.04	84.3	0
CH	CH	961.3	T1T1	698.55	131.4	131.4
C ₆ H ₅	H	465.4	A2H	435.62	29.8	0
C ₆ H ₅ CH ₂	H	367.5	C1H	412.53	-45.0	0

^aCalculated using values from Tables 11 and $\Delta_f H_m^\circ(\text{H}, \text{g}) = 217.999 \text{ kJ} \cdot \text{mol}^{-1}$ and some data from Simões and Beauchamp.¹⁰

^bReorganization of H is considered to be zero.

TABLE 18. Experimental and estimated Cp values for alkanes, alkenes and alkynes

Compound		Gas-phase			Liquid phase		
Formula	Name	Experimental Cp (J·mol ⁻¹ ·K ⁻¹) ^a	Estimated Cp (J·mol ⁻¹ ·K ⁻¹)	Absolute deviation (J·mol ⁻¹ ·K ⁻¹)	Experimental Cp (J·mol ⁻¹ ·K ⁻¹) ^a	Estimated Cp (J·mol ⁻¹ ·K ⁻¹)	Absolute deviation (J·mol ⁻¹ ·K ⁻¹)
alkanes							
CH ₄	methane	35.69	35.7	0.0			
C ₂ H ₆	ethane	52.49	52.5	0.0			
C ₃ H ₈	propane	73.60	74.4	0.8		108.3	
C ₄ H ₁₀	butane	98.49	96.8	1.7		137.5	
	isobutane	96.65	97.7	1.0		137.1	
C ₅ H ₁₂	pentane	120.07	119.2	0.9	167.19	166.8	0.4
	butane, 2-methyl	118.87	120.2	1.4	164.85	164.6	0.2
	propane, 2,2-dimethyl	120.82	120.5	0.3		160.4	
C ₆ H ₁₄	hexane	142.59	141.6	1.0	195.52	196.1	0.6
	pentane, 2-methyl	142.21	142.7	0.5	194.19	193.9	0.3
	pentane, 3-methyl	140.12	142.8	2.7	191.16	192.1	0.9
	butane, 2,2-dimethyl	141.46	143.0	1.5	189.67	188.6	1.1
C ₇ H ₁₆	butane, 2,3-dimethyl	139.41	142.6	3.2	189.02	191.4	2.4
	heptane	165.18	164.0	1.1	224.64	225.4	0.8
	hexane, 2-methyl	164.51	165.1	0.6	222.92	223.1	0.2
	hexane, 3-methyl		165.2			221.4	
	pentane, 3-ethyl	165.98	165.4	0.6	219.58	219.6	0.0
	pentane, 2,2-dimethyl	166.69	165.4	1.3	221.12	217.9	3.3
C ₈ H ₁₈	pentane, 2,3-dimethyl		165.2		218.30	218.9	0.6
	pentane, 2,4-dimethyl	170.75	166.1	4.6	224.32	220.9	3.4
	pentane, 3,3-dimethyl	165.77	165.5	0.3	214.80	216.7	1.9
	butane, 2,2,3-trimethyl	163.26	163.3	0.0	213.51	215.5	2.0
	octane	187.78	186.5	1.3	255.68	254.7	1.0
	heptane, 2-methyl	187.23	187.5	0.3	252.00	252.4	0.4
	heptane, 3-methyl	185.81	187.7	1.9	250.20	250.6	0.4
	heptane, 4-methyl		187.7		251.08	250.6	0.5
	hexane, 3-ethyl	189.62	187.8	1.8		248.9	
	hexane, 2,2-dimethyl		187.8			247.1	
	hexane, 2,3-dimethyl	184.10	187.6	3.5		248.2	
	hexane, 2,4-dimethyl		188.7			248.4	
	hexane, 2,5-dimethyl		188.6		249.20	250.2	1.0
	hexane, 3,3-dimethyl		200.2		246.60	246.6	0.0
	hexane, 3,4-dimethyl	182.34	187.8	5.5		246.4	
	pentane, 3-ethyl, 2-methyl	192.05	187.8	4.3		246.4	
	pentane, 3-ethyl, 3-methyl	187.99	188.0	0.0		244.9	
	pentane, 2,2,3-trimethyl		185.8			242.9	
	pentane, 2,2,4-trimethyl	188.41	188.9	0.5	242.49	244.9	2.4
	pentane, 2,3,3-trimethyl		185.8		245.56	243.6	2.0
	pentane, 2,3,4-trimethyl	191.59	187.6	4.0	247.32	245.8	1.5
	butane, 2,2,3,3-tetramethyl	187.19	187.2	0.0			
alkenes							
C ₂ H ₄	ethene	42.90	42.9	0.0			
C ₃ H ₆	propene	64.32	64.8	0.5		101.9	0.1
C ₄ H ₈	1-butene	85.56	85.6	0.0	128.96	129.0	0.0
	(Z)-2-butene	80.15	79.3	0.9	127	127.1	0.1
	(E)-2-butene	87.67	88.1	0.4		133.7	
	propene, 2-methyl	88.09	88.1	0.0		123.9	
C ₅ H ₁₀	1-pentene	108.2	107.7	0.5	154.87	154.5	0.3
	(Z)-2-pentene	98.8	99.7	0.9	151.8	150.4	1.4
	(E)-2-pentene	108.9	108.5	0.4	157.0	157.0	0.0
	1-butene, 2-methyl	109.96	110.0	0.0	157.3	157.3	0.0
	1-butene, 3-methyl		103.3		156.1	156.1	0.0
	2-butene, 2-methyl	105.02	105.0	0.0	152.8	152.8	0.0
C ₆ H ₁₂	1-hexene		130.1		183.3	183.8	0.5
	(Z)-2-hexene		122.1		178.36	179.7	1.3
	(E)-2-hexene		130.9			186.3	
	(Z)-3-hexene		120.1			173.7	
	(E)-3-hexene		129.0			180.3	
	1-pentene, 2-methyl		132.4			186.6	
	1-pentene, 3-methyl		125.8			183.6	
	1-pentene, 4-methyl		131.2			181.5	
	2-pentene, 2-methyl		125.5			176.1	
	(Z)-2-pentene, 3-methyl		126.9			186.2	
	(E)-2-pentene, 3-methyl		126.9			186.2	
	(Z)-2-pentene, 4-methyl					181.3	
	(E)-2-pentene, 4-methyl					187.9	
	1-butene, 2-ethyl		131.8			193.7	
	1-butene, 2,3-dimethyl		124.3			174.2	
	1-butene, 3,3-dimethyl						

TABLE 18. Experimental and estimated Cp values for alkanes, alkenes and alkynes—Continued

Compound		Gas-phase			Liquid phase		
Formula	Name	Experimental Cp (J·mol ⁻¹ ·K ⁻¹) ^a	Estimated Cp (J·mol ⁻¹ ·K ⁻¹)	Absolute deviation (J·mol ⁻¹ ·K ⁻¹)	Experimental Cp (J·mol ⁻¹ ·K ⁻¹) ^a	Estimated Cp (J·mol ⁻¹ ·K ⁻¹)	Absolute deviation (J·mol ⁻¹ ·K ⁻¹)
	2-butene, 2,3-dimethyl	123.60	123.6	0.0	174.68	174.7	0.0
				alkynes			
C ₂ H ₂	ethyne	44.04	44.0	0.0			
C ₃ H ₄	propyne	60.73	60.5	0.2			
C ₄ H ₆	1-butyne	81.82	80.0	1.9			
	2-butyne	78.82	79.0	0.2			
C ₅ H ₈	1-pentyne	102.56	102.4	0.2			
	2-pentyne	99.59	98.4	1.2			
	1-butyne, 3-methyl	106.09	106.1	0.0			
C ₆ H ₁₀	1-hexyne	125.95	124.8	1.1			
	2-hexyne	119.65	120.9	1.2			
	3-hexyne		117.9				
	1-pentyne, 3-methyl	129.68	129.3	0.4			
	1-pentyne, 4-methyl	126.69	125.9	0.8			
	2-pentyne, 4-methyl	124.44	125.2	0.7			
	1-butyne, 3,3-dimethyl	131.31	131.7	0.4			
C ₇ H ₁₂	1-heptyne	142.99	147.2	4.2			
	2-heptyne		143.3				
	3-heptyne		140.3				
	2-hexyne, 4-methyl	148.04	147.7	0.3			
	2-hexyne, 5-methyl	144.58	144.3	0.3			
	2-pentyne, 4,4-dimethyl	150.56	150.2	0.4			

^aNIST Webbook.¹³

TABLE 19. Parameters obtained for the calculation of Cp values

Parameter	Value for gas phase	Value for liquid phase
C3H	16.61	15.62
C2H	10.46	15.34
C1H	8.97	14.14
C0H	8.92	n.a.
C1C1	-1.30	n.a.
C1C2	-0.18	-3.62
C1C3	0.12	-1.92
C1C4	3.22	-2.31
C2C2	1.50	-1.39
C2C3	1.96	-1.48
C2C4	4.98	-1.20
C3C3	1.34	-1.75
C3C4	2.25	-1.45
C4C4	6.48	n.a.
D1D1	2.17	1.62
D1D2	1.93	5.56
D1D3	-1.17	-0.76
D2D2	3.00	5.16
D2D3	2.41	2.51
D3D3	3.44	2.65
C1D2	5.31	3.48
C1D3	7.55	3.90
C2D2	5.02	-0.28
C2D3	8.68	10.21
C3D2	n.a.	3.49
C3D3	n.a.	n.a.
C4D2	n.a.	n.a.
C4D3	n.a.	n.a.
D1H	10.18	16.04
D2H	10.33	18.38
Z11	-8.81	-6.61
Z14	n.a.	n.a.
Z44	n.a.	n.a.
T1T1	5.54	n.a.
T1T2	8.17	n.a.
T2T2	12.76	n.a.
C1T2	6.23	n.a.
C2T2	4.91	n.a.
C3T2	8.62	n.a.
C4T2	13.93	n.a.
T1H	19.25	n.a.

n.a.—not available.

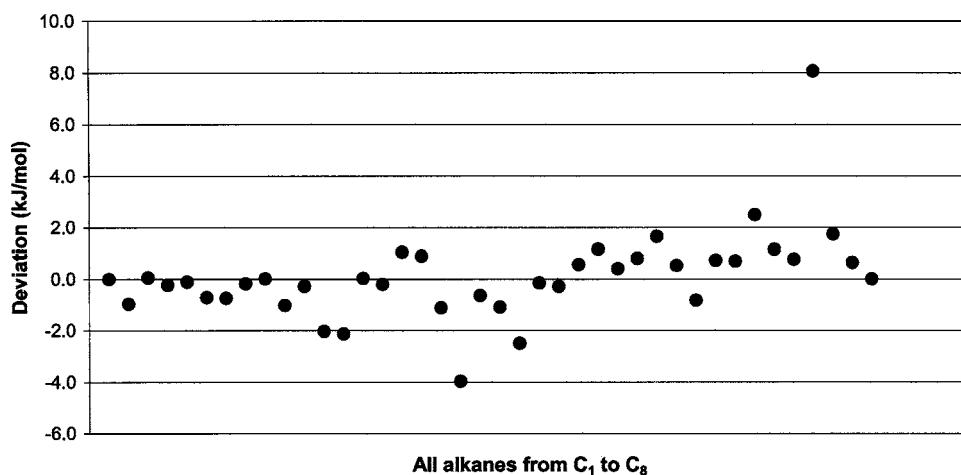


FIG. 15. Deviations between experimental and estimated gas-phase enthalpy of formation for all alkanes from C_1 to C_8 .

7. Acknowledgments

Financial support from Fundação para a Ciência e a Tecnologia, Portugal (Project No. POCTI/199/QUI/35406) is acknowledged. The author acknowledges appreciation to Professor Martinho Simões, Dr. J. Marçalo, and M. Augusta Antunes in reading the paper and giving valuable suggestions to improve it.

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